

Interfacial Oxidation of Ultrathin Nickel and Chromium Films on Yttria-Stabilized Zirconia[†]

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The substrate-induced oxidation upon prolonged annealing in UHV of ultrathin films of Ni and Cr vapor deposited on yttria-stabilized zirconia YSZ(100) was studied by X-ray photoelectron spectroscopy (XPS) to obtain information about the oxidation mechanism, determine the available quantity of reactive oxygen in YSZ, and investigate the thermal stability of the thin oxide films. Up to about 0.8 ML of Ni deposited at room temperature was oxidized to NiO at a constant rate at 650 K via the substrate, whereas at slightly higher coverage, the oxidation rate under identical conditions was drastically reduced. In contrast to Ni, up to 4.8 ML of Cr deposited at 275 K could be oxidized via the substrate to Cr₂O₃ upon extensive UHV annealing at increasing temperature up to 820 K, indicating a reactive oxygen content of at least 4×10^{-6} with respect to the lattice oxygen in the YSZ specimen. The Cr₂O₃ decomposed to metallic Cr above about 800 K, whereas NiO was stable up to the maximum temperature of 875 K. These results indicate that the oxidation via the substrate is kinetically analogous to the gas-phase oxidation of bulk Ni and Cr. The reactive oxygen content of the single-crystal YSZ is larger than expected, and part of it is accommodated at the surface of the substrate. The thermal stability of the thin oxide films is determined by the oxygen exchange with YSZ and not by the respective bulk oxide thermodynamic decomposition temperature.

Introduction

Zirconia is an interesting material for ceramic, optical, and thin film applications. Undoped ZrO₂ is not stable up to its melting point and can crystallize successively into monoclinic, tetragonal, and cubic phases. The cubic phase can be stabilized at all temperatures by the addition of solutes such as CaO, MgO, and Y₂O₃. Zirconia fully stabilized with yttria (YSZ) has good ionic conductivity and is a promising material for oxygen sensors and solid oxide fuel cells (SOFCs).^{1–3} Like other stabilized zirconias, YSZ is known to exhibit an oxygen activity- and temperature-dependent oxygen nonstoichiometry on the order of 10^{-5} with respect to total lattice oxygen, which for pure, single-crystalline materials is mainly attributed to the interaction of oxygen with bulk defects.⁴ This nonstoichiometry is a source of mobile oxygen, which can interact with supported metals such as thin film electrodes or nanometer-sized heterogeneous catalyst particles, thus affecting their electrochemical or catalytic behavior.⁵ Mobile oxygen is transported at elevated temperature via the normal ion conducting oxygen vacancy mechanism for YSZ.⁶

The Ni/YSZ system is interesting both for catalytic and electrochemical applications, and model studies of ultrathin Ni films on single-crystalline YSZ have recently appeared.^{7–10} Submonolayer amounts of Ni on single-crystal yttria-stabilized ZrO₂ (YSZ) were found to be oxidized by extensive annealing in UHV above 480 K^{8,10}, whereas ultrathin NiO films on YSZ surfaces that were extensively annealed in UHV decomposed to metallic Ni upon annealing below the expected thermodynamic dissociation limit for NiO.⁷ The substrate-related origin of these phenomena was supported experimentally by compari-

son with the Ni/ α -Al₂O₃ system, where no such effects were observed under similar conditions.⁹ The proposed interpretation was that YSZ can act both as a source and a sink of reactive oxygen exchanged via the built-in oxygen ion vacancies because the Ni oxidation rate was in agreement with published oxygen transport properties for YSZ.¹⁰ However, the origin and the content of this mobile oxygen in the single-crystal YSZ substrate were not investigated in detail.

The Cr/YSZ(100) system has not been studied so far, although model studies of Cr deposition on various oxides, especially alumina, have drawn considerable attention and have demonstrated strong interfacial interactions due to the high reactivity of Cr.^{11–14} The fact that Cr metal can be oxidized very easily renders ultrathin Cr deposits more appropriate than Ni for titrating excess oxygen in single-crystal YSZ.

This work presents an XPS study of the oxidation, upon heat treatment in UHV, of Ni/YSZ deposits with systematically varying amounts of Ni up to about 1 ML, beyond which the oxidation rate becomes very slow to allow an estimation of the available quantity of excess oxygen in YSZ. For that purpose, thicker, more easily oxidizable Cr/YSZ deposits were studied by XPS under similar conditions. The relative stability of the two metal oxides on YSZ upon annealing in UHV was also investigated.

Experimental Section

The XPS experiments took place in an ultrahigh vacuum chamber (base pressure 5×10^{-10} mbar) using an EA-11 Leybold hemispherical electron-energy analyzer and nonmonochromatized Al K α radiation (1486.6 eV) from a VSW dual-anode X-ray source. The analyzer was operated in constant ΔE mode with 100-eV pass energy resulting in a analyzed area of 3×5 mm², and binding energy values were referenced to 182.6 eV for Zr3d_{5/2}.⁷ The $10 \times 10 \times 0.5$ mm³ YSZ(100) (9% Y₂O₃)

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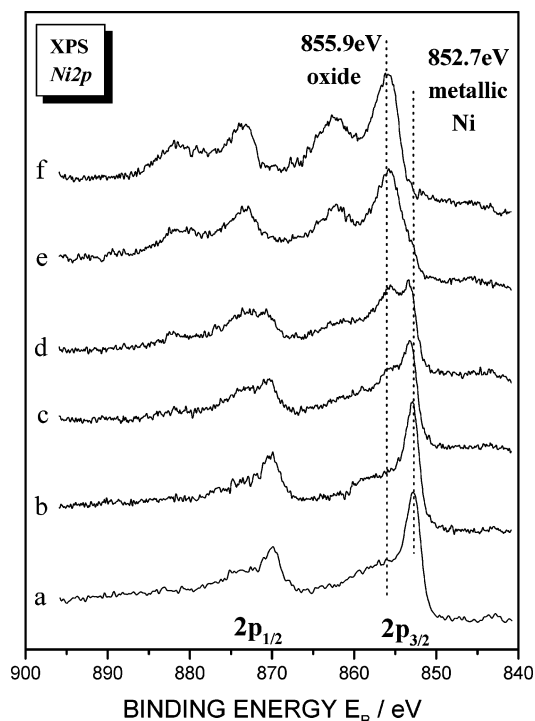


Figure 1. Ni 2p XP spectra for 0.8-ML Ni/YSZ (100) following heating at 650 K in UHV for (a) 8, (b) 21, (c) 70, (d) 98, (e) 177, and (f) 230 min.

substrate crystals (Mateck, Germany) were mounted on a Mo plate, which could be heated to 1160 K, corresponding to a calibrated maximum specimen surface temperature of 875 K.¹⁰ In situ specimen cleaning from adventitious carbon prior to each Ni deposition was achieved by 2.5-keV Ar⁺ sputtering followed by 15 min of annealing at 650 K in 5×10^{-6} mbar O₂, leading to an O 1s/Zr 3d XPS intensity ratio on the clean surface of 0.79 ± 0.01 . Prior to Cr deposition, the specimen was cleaned by 1.5-keV ion sputtering from a N₂/O₂/Ar mixture followed by short UHV annealing at 800 K, leading to an O 1s/Zr 3d XPS intensity ratio on the clean surface of 0.84 ± 0.01 . Nickel and chromium were uniformly deposited on the top surface of the specimen slab from electron-beam evaporation sources at specimen temperatures of ~ 330 K (near room temperature) and 275 K (liquid-nitrogen cooling), respectively. The deposited metal coverage in equivalent monolayers (1 ML $\approx 2 \times 10^{15}$ atoms/cm² for both metals) was estimated by calibrating the e-beam evaporator flux doses from the exponential attenuation of the Zr 3d substrate XPS intensity assuming nearly layerlike growth in submonolayer deposits and a constant metal sticking coefficient.

Results and Discussion

Ni/YSZ. Figure 1 shows a series of Ni 2p XP spectra for 0.8 ML of Ni deposited on clean YSZ (O 1s/Zr 3d = 0.80) at 330 K followed by heating in UHV for increasing periods of time at 650 K in front of the X-ray gun. It is clear that Ni is gradually oxidized and that the process is complete after 230 min. The oxidation is evidenced initially by a broadening of the peaks and then by the gradual replacement of the Ni 2p_{3/2} peak at 852.7 eV, corresponding to dispersed metallic Ni, by a new peak at 855.9 eV with a pronounced satellite at ~ 862 eV, corresponding to a thin NiO layer. The substrate-induced oxidation has been previously observed for ~ 0.2 ML of Ni/YSZ(100) at 635 K in UHV.^{8–10} The experiment of Figure 1 was repeated for a series of Ni deposits on clean YSZ with O

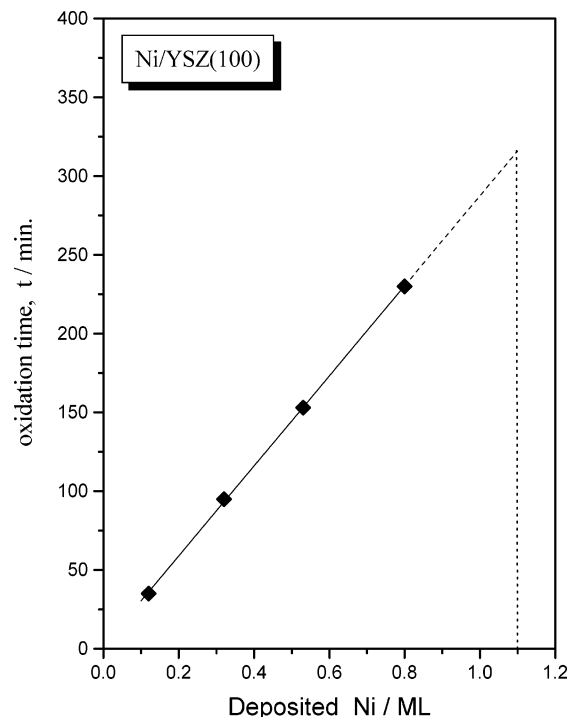


Figure 2. Time for the complete oxidation of Ni deposits annealed in UHV at 650 K versus Ni coverage (0.1–0.8 ML).

1s/Zr 3d = 0.80 ± 0.01 , with increasing Ni coverage from 0.13 to 0.53 ML. During heating at 650 K, the specimen was kept in front of the X-ray gun, and XPS data were taken periodically to follow the oxidation. Figure 2 shows the time required for complete oxidation at 650 K versus Ni coverage up to 0.8 ML. Oxidation time increases linearly with coverage, indicating that for a given rate of oxygen supply to the substrate surface the oxidation probability does not depend on the Ni coverage. Remarkably, when the experiment was repeated for Ni coverages above 1 ML, as shown in Figure 3 for 1.1 ML of Ni, the oxidation rate appeared to decrease drastically. Instead of complete oxidation within about 300 min, as predicted by Figure 2, only a small broadening of the Ni 2p peaks could be observed in Figure 3 even after 520 min at 650 K under the same conditions.

The source of the oxygen species responsible for Ni oxidation under the experimental conditions of Figures 1 and 2 cannot be the lattice oxygen because breaking the strong Zr–O and Y–O bonds is unlikely. Reduced cationic species leading to even slight changes in the Zr or Y XPS peak shape were never detected at the YSZ surface, whereas internal YSZ discoloration associated with additional O^{2–} vacancies was not observed. The presence of oxygen nonstoichiometry on the order of 10^{-5} (ref 4) can account for the active species because the O atoms necessary to oxidize 0.8 ML of Ni on the top a 1-cm² surface of our specimens ($\sim 1.6 \times 10^{15}$ atoms) constitute only a fraction (0.7×10^{-6}) of the total number of lattice oxygen ions in the specimen (2.6×10^{21} O^{2–}). Because the YSZ crystals were exposed during cleaning to conditions of relatively higher oxygen activity and temperature, they have stored a certain amount of oxygen, which under conditions of UHV and lower temperature becomes a metastable oxygen excess in the bulk of the crystal.⁴ An additional possibility for excess oxygen accommodation would be, of course, in an adsorbed state at the external surface of the YSZ. On the basis of the dimensions of our crystals, their external surface (2.2 cm²) could accommodate excess oxygen on the order of 10^{-6} . Good experimental

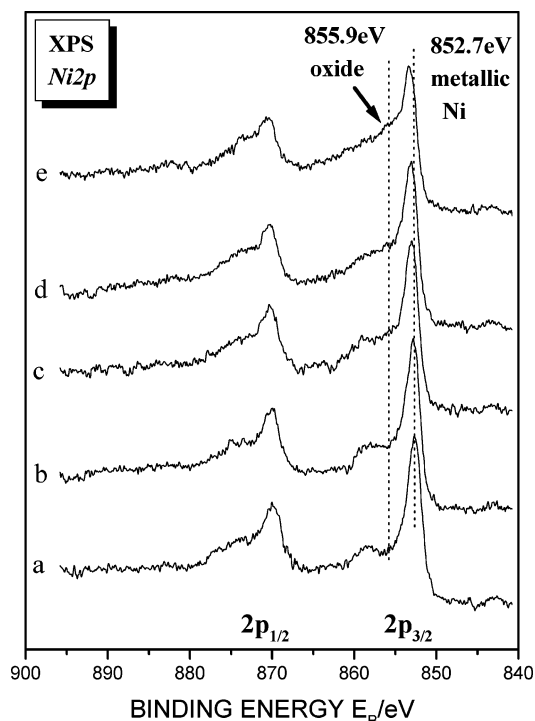


Figure 3. Ni 2p XPS spectra for 1.1-ML Ni/YSZ (100) following heating at 650 K in UHV for (a) 8, (b) 216, (c) 387, (d) 425, and (e) 520 min.

evidence for the ability of the YSZ surface to accommodate additional oxygen is obtained from the observed O 1s/Zr 3d ratio by XPS. After the cleaning treatment under oxidizing conditions, this ratio was about 0.80–0.84, whereas prolonged annealing of YSZ in UHV combined with pure Ar⁺ sputtering can lower this ratio to about 0.65, without any traces of Zr or Y reduction.¹⁰

The transport of excess oxygen can take place via the free oxygen vacancies of YSZ at temperatures higher than about 480 K.⁶ The transport of mobile O²⁻ to the surface of YSZ when the specimen is kept in front of the X-ray gun is not simply diffusive but is enhanced by the positive charging of the surface as a result of photoemission.¹⁰ The charge is neutralized mainly by an O²⁻ ion current on the order of nA flowing between the bottom side of the YSZ crystal in contact with the grounded heating plate and that of the Ni-deposited surface. A simple calculation based on the oxidation time versus Ni coverage data of Figure 2 demonstrates that a current of about 30 nA evenly distributed across the specimen surface is sufficient to provide the necessary O²⁻, assuming that all ions arriving at the surface diffuse and react with the Ni islands (unity oxidation probability). This current value is reasonable for the conditions of the XPS measurements in Figure 2, suggesting that the oxidation probability is near unity. For comparison, if oxidation had taken place via dissociative chemisorption of gas-phase O₂ with a sticking coefficient of unity on Ni and negligible diffusive flux from the substrate (oxidation probability proportional to Ni coverage), then it would be straightforward to calculate that complete oxidation for all experimental points in Figure 2 corresponding to an O₂ exposure of ~2 langmuirs (1 langmuir = 1.33 × 10⁻⁶ mbar s).

The negligible oxidation rate above 1 ML of Ni (Figure 3) does not signify a limit in the available excess oxygen but rather a drastic decrease in the efficiency of arriving ions to oxidize Ni. This would be equivalent to the well-known lowering of the reactive sticking coefficient in bulk Ni surface oxidation

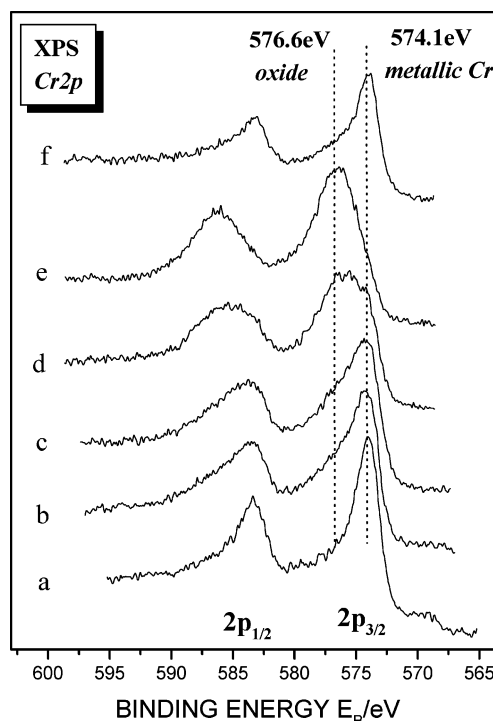


Figure 4. Cr 2p XPS spectra for 4.8-ML Cr/YSZ (100) (a) as deposited at 275 K, (b) after 200 min at 350 K with intermediate 20-min annealings in UHV at 415, 485, and 550 K, (c) after 120 min at 550 K with intermediate 20-min annealing at 615 K, (d) after an additional 120 min at 550 K with intermediate 20-min annealings at 685 and 750 K, (e) after an additional 60 min at 550 K with intermediate 20-min annealing at 815 K, and (f) after 20 min of annealing at 875 K.

via the gas phase, whereby the first atomic layer is oxidized quickly (<10 langmuirs), whereas incorporation into the next two or three layers is severely hindered and requires tens of langmuirs.¹⁵ This observation suggests that the oxidation of deposited Ni films via transported ions is kinetically analogous to gas-phase oxidation; that is, single-layer Ni deposits are oxidized very quickly (reaction probability near unity or equivalent gas-phase exposures on the order of 2 langmuirs), whereas with increasing Ni coverage, the appearance of 3-D particles retards oxidation. This retardation is farther enhanced by the tendency of the film to coalesce upon initial heating at 650 K, before oxygen incorporation into the film has time to proceed. Once larger 3-D Ni particles are formed, chemisorption on their surface does not immediately lead to oxidation, as was the case for single-layer islands (Figure 2).

Cr/YSZ. To titrate the available quantity of excess oxygen in the YSZ specimens, it is necessary to let the transported oxygen react with another, more easily oxidizable metal. Chromium is much more reactive than nickel because adsorbing oxygen atoms tend to dissolve in the inner layers instead of staying strongly chemisorbed at the surface and inhibiting further oxidation.¹⁶

To study the Cr/YSZ(100) interfacial interaction, 4.8 ML of Cr was vapor deposited onto a sputter-cleaned YSZ (100) single crystal at a specimen temperature of 275 K to achieve a good dispersion of the deposit and to minimize interfacial interactions during deposition. Because sputtering was carried out in an Ar/air mixture, the initial value of the O 1s/Zr 3d ratio was 0.84 ± 0.01, which is larger than in the case of Ni deposition, indicating some excess oxygen in the YSZ surface region prior to Cr deposition. The temperature was then increased gradually, keeping the specimen in front of the X-ray gun, to monitor periodically the progress of oxidation by XPS. Figure 4 shows

a series of Cr 2p XPS spectra, starting with that taken immediately after deposition at 275 K (spectrum a) and followed by a series of spectra taken after thermal treatment at gradually increasing temperature up to 875 K. Immediately after deposition, the Cr 2p XPS doublet is characterized by narrow peaks with Cr 2p_{3/2} at a binding energy of 574.1 eV, corresponding to metallic Cr. With increasing time at elevated temperatures in front of the X-rays, it is clear that Cr is gradually oxidized and that the process is nearly complete in spectrum e after several hours at temperatures between 350 and 815 K. The oxidation is evidenced initially by a broadening of the peaks and then by the gradual replacement of the metallic Cr 2p_{3/2} peak at 574.1 eV by a new peak at 576.6 eV corresponding to Cr₂O₃.¹⁴ Because the number of O atoms necessary to oxidize ~80% of the 4.8 ML of Cr on the top specimen surface is 1.1×10^{16} , we can conclude that the excess oxygen content was at least 4×10^{-6} , which reflects the change in oxygen nonstoichiometry between UHV and the oxidizing conditions during the cleaning of the crystal (reactive sputtering in the Ar/air mixture). A substantial fraction of this amount could be accommodated near the top surface region of the YSZ crystal, which initially exhibited an enhanced O 1s/Zr 3d intensity ratio. Recent literature data for the nonstoichiometric oxygen content, δ , in polycrystalline YSZ in the range of temperature and oxygen pressures of this work (up to 875 K and from UHV up to 5×10^{-6} mbar of O₂) report a value of $\sim 1 \times 10^{-6}$, measured at 600 K by electrochemically driving excess oxygen out of the crystal into the vacuum and using mass spectrometry.⁵ There are also gravimetric determinations of δ for 4% CaO-stabilized zirconia covering the above pressure range but at much higher temperature, 1500 to 1600 K, which yield an increase in δ , between UHV and 5×10^{-6} mbar of O₂, of not more than $\sim 2 \times 10^{-6}$.⁴ The larger value observed in the present work can be at least partially accounted for by excess oxygen accommodated in the surface region.

Spectrum f in Figure 4 shows that the Cr₂O₃ formed via the excess mobile oxygen is not stable upon annealing at 875 K and is reduced to metallic Cr. This effect will be discussed farther in the following section, in comparison with the behavior of NiO under similar conditions.

Thermal Stability of Ultrathin Cr₂O₃ and NiO Layers on YSZ. Figure 5 shows a series of Cr 2p spectra taken at 550 K for the same 4.8-ML Cr deposit of the previous section, following the last spectrum (f) in Figure 4. Spectrum a in Figure 5, obtained after 30 min in UHV at 550 K in front of the X-rays, is still predominantly metallic Cr. Compared with the initially deposited Cr at 275 K, the deposit has coalesced into larger 3-D particles, as evidenced by the decrease of the Cr 2p/Zr 3d intensity ratio from 2.0 to 1.14. The O 1s/Zr 3d ratio at this point is 0.89 compared with a ratio of 0.84 prior to Cr deposition, indicating that the oxidation process via the substrate has already been initiated. Spectrum b, obtained after 700 langmuirs of exposure to 1×10^{-6} mbar O₂ at 550 K, shows the complete oxidation of the film to Cr₂O₃. Spectra c–e were taken after three successive 20-min annealings at 780 K in UHV and show that the decomposition of the oxide has started but is not completed at this temperature. Upon subsequent 20-min annealings at 815 and 875 K in UHV (spectra f and g), the oxide was completely reduced to metallic Cr. At this point, the O 1s/Zr 3d ratio was 0.93, compared with a ratio of 0.84 prior to Cr deposition. It is interesting that when the original Cr deposit was oxidized by the substrate the oxide was stable up to 815 K (Figure 4, spectrum e); however, it should be taken into account that the dispersion of the oxidized film in the latter

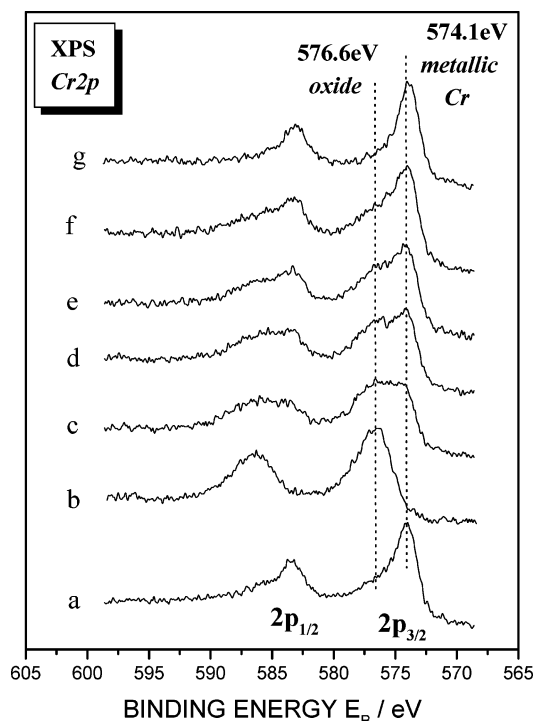


Figure 5. Cr 2p XPS spectra for 4.8-ML Cr/YSZ (100) (a) as in Figure 4f after annealing at 550 K in UHV for 30 min, (b) after exposure to 700 langmuirs of O₂ at 550 K, (c–e) after annealing at 780 K in UHV for 20, 40, and 60 min, respectively, (f) after annealing at 815 K in UHV for 20 min, and (g) after annealing at 875 K in UHV for 20 min.

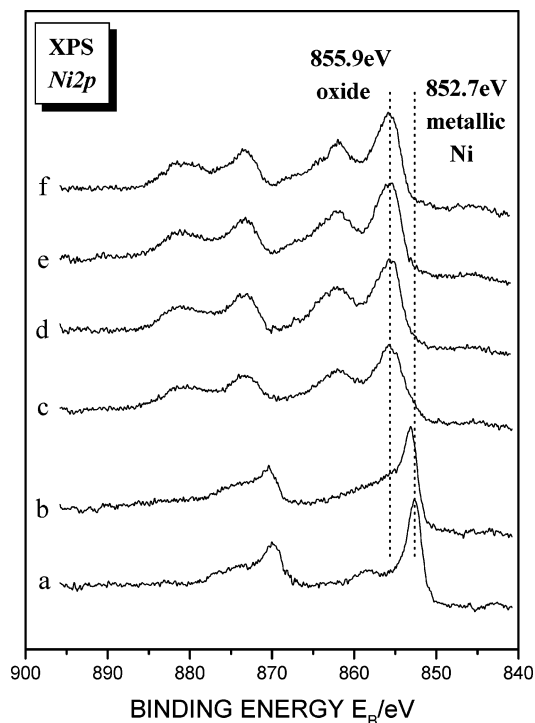


Figure 6. Ni 2p XPS spectra for 1.1-ML Ni/YSZ (100) (a, b) following heating at 650 K in UHV for 8 and 520 min, respectively, (c) after exposure to 9000 langmuirs of O₂ at 340 K, and (d–f) after subsequent annealings for 30 min in UHV at 760, 825, and 875 K, respectively.

case was higher than in the case of Figure 5, suggesting that increased oxide dispersion enhances thermal stability.

Figure 6 shows a series of Ni 2p spectra taken at 650 K for the 1.1-ML Ni deposit (Figure 3). Spectra a and b in Figure 6 are the same as spectra a and e in Figure 3, respectively, and demonstrate that after 520 min of annealing at 650 K Ni

oxidation has not proceeded significantly. Spectrum c, obtained after 9000 langmuirs of exposure to 5×10^{-6} mbar O_2 at 340 K, shows the complete oxidation of the film to NiO. Spectra d–f were taken after three successive 30-min annealings at 760, 825, and 875 K in UHV and show that NiO remains stable up to the maximum temperature.

The higher thermal stability of nickel oxide is rather unexpected in comparison with that of chromium (Figure 5). Bulk Cr_2O_3 is thermodynamically much more stable than NiO (decomposition oxygen pressure at 920 K on the order of 10^{-31} mbar for Cr_2O_3 versus 10^{-15} mbar for NiO); therefore, its decomposition at lower temperature in the same UHV environment must be mediated by the substrate. It has been previously reported that NiO on YSZ(100) may also decompose at temperatures as low as 740 K in UHV if the O 1s/Zr 3d ratio on the YSZ surface drops below about 0.7.¹⁰ However, in the present case, the O 1s/Zr 3d ratio in the experiments with Cr was always larger than in those with Ni (0.84 versus 0.80). The facilitated decomposition of the oxide reflects the ability of the YSZ to accommodate the evolving oxygen in the bulk and on its surface. The latter is consistent with the increased O 1s/Zr 3d ratios after the oxide decomposition, compared with the corresponding ratio on the clean YSZ. Thus, the thermodynamics of the nonstoichiometric oxygen accommodation/desorption process determines the decomposition temperature of oxides dispersed on YSZ, regardless of their bulk thermal stability. Consistent with this is the recently reported observation⁵ that excess oxygen desorption from YSZ in UHV starts around 800 K, which is also the temperature at which Cr_2O_3 begins to decompose. The enhanced thermal stability of NiO versus Cr_2O_3 is attributed to the same physical reason that makes Ni more difficult to oxidize than Cr, namely, the fact that oxygen can be more easily transported to (and hence from) the bulk of Cr metal compared with Ni.

Conclusions

Ultrathin Ni and Cr films deposited on YSZ(100) were oxidized upon annealing above 550 K in UHV by excess reactive oxygen stored in the substrate and transported to the surface. Nickel oxidation proceeded quickly up to about a

monolayer coverage and then was drastically retarded, in contrast to chromium oxidation, which proceeded relatively quickly even up to 4.8 ML. This behavior is analogous to the well-known gas-phase oxidation mechanisms for bulk Ni and Cr.

Monitoring the extent of Cr oxidation can be used as a simple method to determine the reactive or nonstoichiometric oxygen content of the single-crystal YSZ. In the present case, a value of $\sim 4 \times 10^{-6}$ was obtained, which is significantly larger than a recently measured value in polycrystalline YSZ. The results suggest that a significant part of this oxygen is accommodated in the surface of YSZ.

The thermal stability of thin oxide films on YSZ is not determined by their thermodynamically derived decomposition oxygen pressure but is limited by the interaction with the substrate. Oxygen is released via its accommodation at the YSZ surface and at bulk centers of excess oxygen storage. The onset of Cr_2O_3 decomposition occurs at the temperature where excess oxygen from YSZ begins to desorb into UHV.

References and Notes

- (1) Etsell, T. H.; Flengas, S. N. *Chem. Rev.* **1970**, *70*, 339.
- (2) Badwal, S. P. S. *Solid State Ionics* **1992**, *52*, 23.
- (3) Minh, N. Q. *J. Am. Ceram. Soc.* **1993**, *76*, 563.
- (4) Xue, J.; Dieckman, R. *Solid State Ionics* **1994**, *73*, 273.
- (5) Katsaounis, A.; Nikopoulou, Z.; Verykios, X. E.; Vayenas, C. G. *J. Catal.* **2004**, *222*, 192.
- (6) Manning, P. S.; Sirman, J. D.; De Souza, R. A.; Kilner, J. A. *Solid State Ionics* **1997**, *100*, 1.
- (7) Zafeirotos, S.; Kennou, S. *Surf. Sci.* **2001**, *482–485*, 266.
- (8) Zafeirotos, S.; Kennou, S. *Surf. Sci.* **2003**, *532–535*, 402.
- (9) Sygellou, L.; Zafeirotos, S.; Tsud, N.; Matolin, V.; Kennou, S.; Ladas, S. *Surf. Interface Anal.* **2002**, *34*, 545.
- (10) Sygellou, L.; Ladas, S. *Surf. Sci.*, in press, 2004.
- (11) Lu, H.; Shen, D. H.; Bao, C. L.; Wang, Y. X. *Phys. Status Solidi* **1997**, *159*, 425.
- (12) Spolveri, I.; Atrei, A.; Cortigiani, B.; Bardi, U.; Santucci, A.; Ghisletti, D. *Surf. Sci.* **1998**, *412–413*, 631.
- (13) Hu, M.; Noda, S.; Komiyama, H. *J. Appl. Phys.* **2003**, *93*, 9336.
- (14) Sainio, J.; Eriksson, M.; Lahtinen, J. *Surf. Sci.* **2003**, *532–535*, 396.
- (15) Wang, W.-D.; Wu, N. J.; Thiel, P. A. *J. Chem. Phys.* **1990**, *92*, 2025.
- (16) Gewinner, G.; Peruchetti, J. C.; Jaegle, A.; Kalt, A. *Surf. Sci.* **1978**, *78*, 439.