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Abstract

Transition metal catalysts such as Rh/Pt used in a three-way automotive catalytic converter have to perform reduction and oxidation functions at the same time. This can be accomplished only in a specific range of oxygen pressure and temperature. In order to maintain a constant partial pressure of oxygen in the vicinity of catalysts mixtures of ceria and zirconia are used. Ceria is an essential component due to its capability of storing oxygen under oxidizing and releasing oxygen under reducing conditions. However, this function deteriorates with time and eventually a catalytic converter stops working properly. It is not well understood why this particular mixture of oxides can achieve the role as a oxygen buffer and why its lifetime is limited. In order to address this issue and to understand the structural interplay at the ceria/zirconia interface, we studied the atomic structure of ultra-thin ceria layers deposited on single crystals of (001) oriented Y-stabilized zirconia (YSZ), *in situ*, during annealing in air using the synchrotron x-ray surface diffraction technique.

Disciplines

Automotive Engineering | Biochemical and Biomolecular Engineering | Catalysis and Reaction Engineering | Ceramic Materials | Chemical Engineering | Engineering

Comments

The volume in which this report appeared no. 73 in a larger series known as Ceramic Transactions.

ULTRA-THIN CeO₂ OVERLAYER ON YSZ STUDIED BY X-RAY SURFACE SCATTERING

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INTRODUCTION

Transition metal catalysts such as Rh/Pt used in a three-way automotive catalytic converter have to perform reduction and oxidation functions at the same time. This can be accomplished only in a specific range of oxygen pressure and temperature. In order to maintain a constant partial pressure of oxygen in the vicinity of the catalysts mixtures of ceria and zirconia are used. Ceria is an essential component due to its capability of storing oxygen under oxidizing and releasing oxygen under reducing conditions. However, this function deteriorates with time and eventually a catalytic converter stops working properly. It is not well understood why this particular mixture of oxides can achieve the role as a oxygen buffer and why its lifetime is limited. In order to address this issue and to understand the structural interplay at the ceria/zirconia interface, we studied the atomic structure of ultra-thin ceria layers deposited on single crystals of (001) oriented Y-stabilized zirconia (YSZ), *in situ*, during annealing in air using the synchrotron x-ray surface diffraction technique.

Scattering intensity in the surface diffraction experiments is low since the scattering volume is limited to few atomic layers at the surface. To overcome this difficulty we applied, for the first time, the energy dispersive mode of x-ray diffraction [1,2,3] in the surface scattering experiment [4]. This method uses a white radiation source, and the structural information is obtained by the spectroscopy of the diffracted x-rays measured at a fixed diffraction angle. The spectrum of the diffracted x-rays is obtained by the use of a solid state detector, such as an intrinsic Ge or Li-drifted Si detector, combined with a multi-channel pulse height analyzer (MCA).

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EXPERIMENTAL METHODS

Sample preparation

The films were prepared by vapor deposition of cerium metal on a 0.7x0.7x0.1 mm single crystal of YSZ, oriented in the (001) direction. Deposition was performed with the zirconia substrate at room temperature in a standard bell jar at a pressure of 10^{-7} Torr, using a tungsten boat for the cerium metal. The metal coverage was targeted to be 1.5×10^{15} atoms/cm², determined using a quartz crystal film thickness monitor.

X-ray diffraction

The synchrotron x-ray scattering experiment was performed at the National Synchrotron Light Source (NSLS) of the Brookhaven National Laboratory beam line X-7A with the grazing angle incidence, in the evanescent wave scattering geometry. We have applied the energy dispersive method for the first time to study scattering from the surface. The scattering vector \mathbf{Q} is related to the photon energy via:

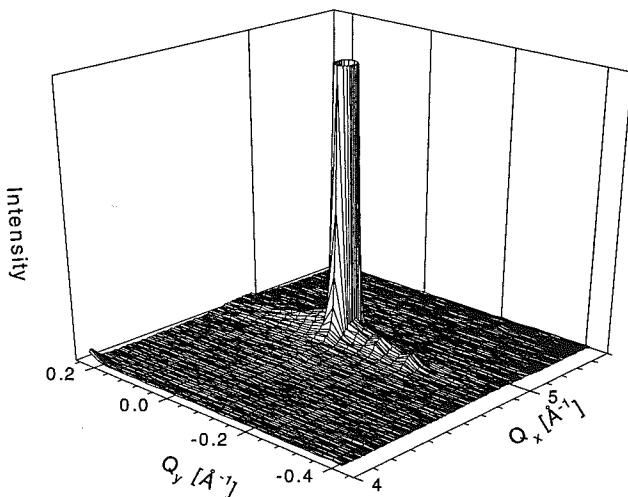


Figure 1. Diffraction pattern near the (400) zirconia Bragg peak at 100°C.

$$Q = \frac{4\pi}{hc} \cdot \sin\theta \cdot E,$$

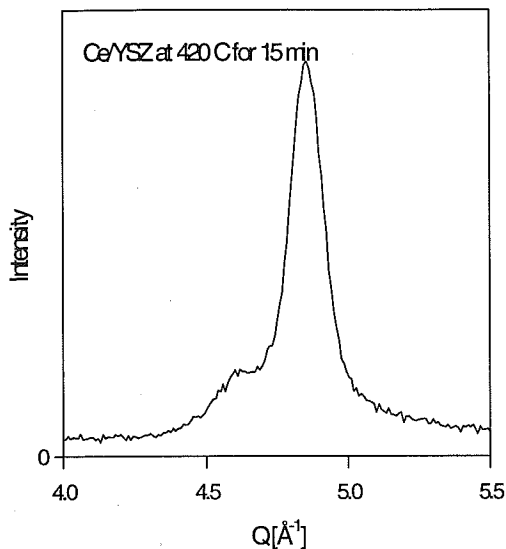


Figure 2. Diffraction intensity near the (400) peak for Ce/YSZ sample annealed at 420°C for 15 minutes. Diffraction was recorded at $Q_y = 0.1 \text{ \AA}^{-1}$ to avoid the diffraction from the YSZ truncation rod. The main peak at 4.8 \AA is a tail of the truncation rod. The shoulder at 4.6 \AA is due to the Ce overlayer.

changes with temperature. Figure 1 shows a 2-d diffraction pattern in the sample plane with both initial and final angles that x-rays make with the sample surface set for subcritical values, about 0.2° . The strongest feature is the surface truncation diffraction rod from the zirconia (400) Bragg peak. From the width of the diffraction peak in Q_x we can deduce the lateral coherence length. At this temperature, apart from the rod, we can observe only the diffraction from the zirconia/film interface which shows up as a ridge extending from the Bragg peak. We believe that after cerium metal was deposited, amorphous or polycrystalline cerium hydroxide is formed which produces only very weak diffuse scattering. After annealing at 420°C we start to see weak diffraction from the ceria (400) peak at $Q_x = 4.6 \text{ \AA}^{-1}$ as

where 2θ is the angle between the incident and scattered beams. Our experimental geometry was typical for the surface scattering study, with the scattering vector nearly in the plane of the sample. The scattering angle 2θ was adjusted to avoid overlapping of fluorescence lines with the Bragg peaks. The sample was oriented with the [1 0 0] direction nearly along the scattering vector, with the z-axis perpendicular to the surface.

RESULTS

The samples were placed on a heater and were annealed in air during the x-ray scattering measurement to observe structural

shown in Fig. 2. This value of Q_x is very close to that expected for pure CeO_2 . This measurement was made at $Q_y = 0.1 \text{ \AA}^{-1}$ to avoid the strong scattering due to the zirconia rod shown in Fig. 1. Most probably hydroxide formed after deposition is crystallizing at this temperature. The width of the ceria peak suggests a lateral coherence length of about 20 \AA .

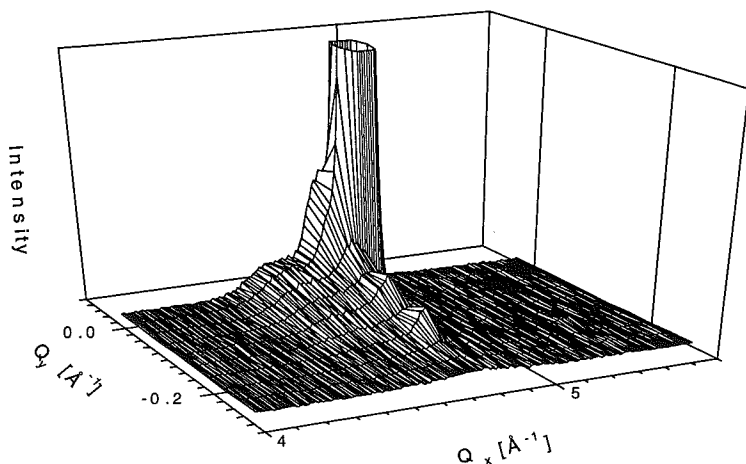


Figure 3. Ce/YSZ at 520°C . Diffraction shows a part of a (400) zirconia rod. The ridge at $Q_x = 4.6 \text{ \AA}^{-1}$ represents scattering from the ceria film.

Further annealing at 520°C results in growth of the ceria peak intensity as illustrated in the Fig. 3. This is accompanied by an increase in the lateral coherence length to about 32 \AA . The diffraction intensity of ceria saturates at this temperature which indicates that all hydroxide has crystallized. If we compare the position of the diffraction ridge coming from the interface in the Figures 1 and 3 we can see that it moved away from the diffraction rod towards a smaller value of Q_x . This indicates that lattice expansion is taking place on the surface of zirconia, possibly due to the inclusion of Ce. At 620°C the ceria diffraction peak moves towards a higher value of Q_x which means that the ceria lattice constant is shrinking, probably signaling the intermixing with zirconia. The width of the ceria peak at this temperature is decreasing and the lateral coherence length of ceria is increased up to 46 \AA . At this stage, most likely, some of ceria grains are growing at the expense of others. Finally annealing above 700°C for a prolonged time leads to Ce diffusion into the bulk of YSZ and gradual disappearance of a ceria diffraction peak as

shown in the Fig. 4. Figure 5 shows a 2-dimensional diffraction intensity map at 740°C after the disappearance of the CeO₂ (400) peak.

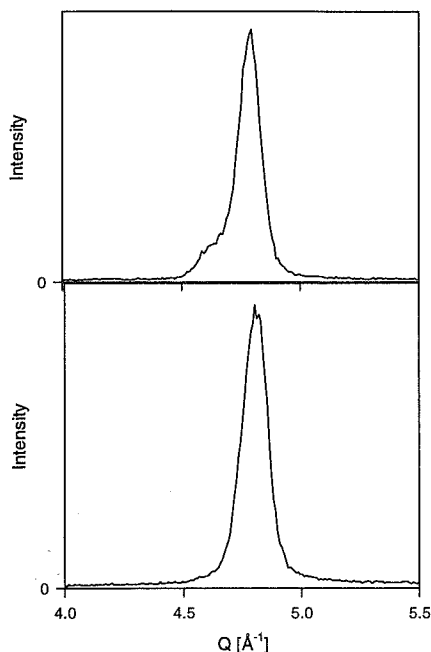


Figure 4. Ce/YSZ at 740°C. Diffraction is measured 0.1 Å away from the zirconia (400) rod. The top figure is measured after 1 hour and the bottom one after 2 hours at 740°C.

CONCLUSIONS

We have demonstrated that with the use of synchrotron radiation the energy dispersive mode can be successfully used in the *in-situ* surface diffraction studies of a changing interface and a thin deposited film. Our study shows that a CeO₂ epitaxial overlayer can easily be formed on a Y stabilized cubic zirconia by simple oxidation of Ce metal layer deposited on the surface. The lattice constant mismatch most likely induces formation of contiguous ceria islands. This microstructure of ceria may be important for catalytic function of ceria/zirconia interface. Cracks and grain boundaries of ceria can provide less stable surfaces and easy passage for oxygen and allow ready exchange of oxygen atoms near the surface. *In-situ* studies of a deposited cerium metal layer show the following evolution with temperature:

- Crystallization of ceria starts at 420°C.
- At 520°C crystallization is completed and interface is modified.
- At 620°C preferential growth of some ceria grains occurs.
- At 720°C cerium diffuses into the bulk.

The preferential growth of some ceria grains modifies the surface microstructure which in turn can deteriorate its efficiency as an oxygen buffer. Prolonged annealing at temperatures above 700°C leads to the diffusion of ceria into the bulk.

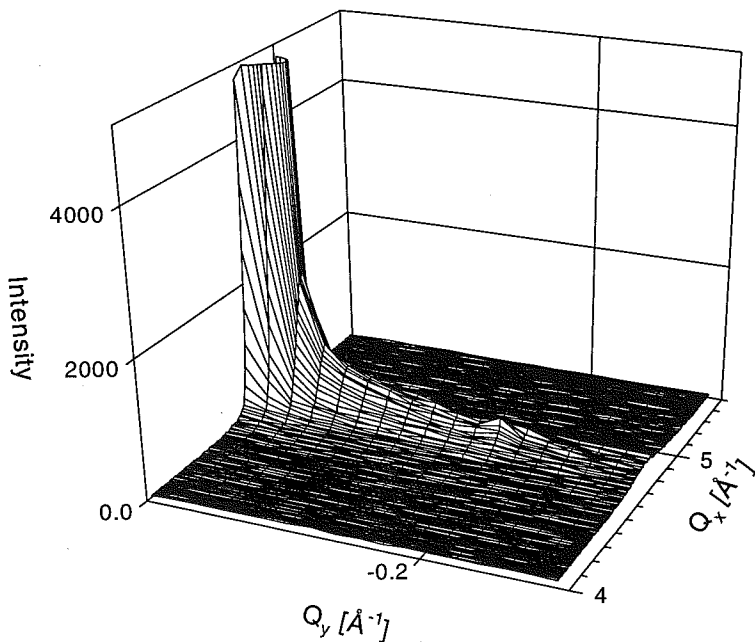


Figure 5. Ce/YSZ at 740°C after prolonged annealing. The ridge from ceria film has disappeared.

ACKNOWLEDGMENTS

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