Advanced Ceramic Coatings and Interfaces V
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Advanced Ceramic Coatings and Interfaces V

A Collection of Papers Presented at the 34th International Conference on Advanced Ceramics and Composites
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The Symposium on Advanced Ceramic Coatings for Structural, Environmental and Functional Applications was held at the 34th Cocoa Beach International Conference on Advanced Ceramics and Composites in Cocoa Beach, Florida, during January 24–29, 2010. A total of 52 papers, including 15 invited talks, were presented at the symposium, covering broad ceramic coating and interface topic areas and emphasizing the latest advancement in coating processing, characterization and development.

The present volume contains fifteen contributed papers from the symposium, with topics including advanced coating processing, advanced coating for wear, corrosion, and oxidation resistance, and thermal and mechanical properties, highlighting the state-of-the-art ceramic coatings technologies for various critical engineering applications.

We are greatly indebted to the members of the symposium organizing committee, including Uwe Schulz, Yutaka Kagawa, Rodney Trice, Irene Spitsberg, Dileep Singh, Brain Hazel, Robert Vaßen, Sophoclis Patsias, Yong-Ho Sohn, Ping Xiao, and Jung Xu, for their assistance in developing and organizing this vibrant and cutting-edge symposium. We also would like to express our sincere thanks to manuscript authors and reviewers, all the symposium participants and session chairs for their contributions to a successful meeting. Finally, we are also grateful to the staff of The American Ceramic Society for their efforts in ensuring an enjoyable conference and the high-quality publication of the proceeding volume.

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Introduction

This CESP issue represents papers that were submitted and approved for the proceedings of the 34th International Conference on Advanced Ceramics and Composites (ICACC), held January 24–29, 2010 in Daytona Beach, Florida. ICACC is the most prominent international meeting in the area of advanced structural, functional, and nanoscopic ceramics, composites, and other emerging ceramic materials and technologies. This prestigious conference has been organized by The American Ceramic Society’s (ACerS) Engineering Ceramics Division (ECD) since 1977.

The conference was organized into the following symposia and focused sessions:

- Symposium 1: Mechanical Behavior and Performance of Ceramics and Composites
- Symposium 2: Advanced Ceramic Coatings for Structural, Environmental, and Functional Applications
- Symposium 3: 7th International Symposium on Solid Oxide Fuel Cells (SOFC): Materials, Science, and Technology
- Symposium 4: Armor Ceramics
- Symposium 5: Next Generation Bioceramics
- Symposium 6: International Symposium on Ceramics for Electric Energy Generation, Storage, and Distribution
- Symposium 7: 4th International Symposium on Nanostructured Materials and Nanocomposites: Development and Applications
- Symposium 8: 4th International Symposium on Advanced Processing and Manufacturing Technologies (APMT) for Structural and Multifunctional Materials and Systems
- Symposium 9: Porous Ceramics: Novel Developments and Applications
- Symposium 10: Thermal Management Materials and Technologies
- Symposium 11: Advanced Sensor Technology, Developments and Applications
Focused Session 1  Geopolymers and other Inorganic Polymers
Focused Session 2  Global Mineral Resources for Strategic and Emerging Technologies
Focused Session 3  Computational Design, Modeling, Simulation and Characterization of Ceramics and Composites
Focused Session 4  Nanolaminated Ternary Carbides and Nitrides (MAX Phases)

The conference proceedings are published into 9 issues of the 2010 Ceramic Engineering and Science Proceedings (CESP); Volume 31, Issues 2–10, 2010 as outlined below:

- Mechanical Properties and Performance of Engineering Ceramics and Composites V, CESP Volume 31, Issue 2 (includes papers from Symposium 1)
- Advanced Ceramic Coatings and Interfaces V, Volume 31, Issue 3 (includes papers from Symposium 2)
- Advances in Solid Oxide Fuel Cells VI, CESP Volume 31, Issue 4 (includes papers from Symposium 3)
- Advances in Ceramic Armor VI, CESP Volume 31, Issue 5 (includes papers from Symposium 4)
- Advances in Bioceramics and Porous Ceramics III, CESP Volume 31, Issue 6 (includes papers from Symposia 5 and 9)
- Nanostructured Materials and Nanotechnology IV, CESP Volume 31, Issue 7 (includes papers from Symposium 7)
- Advanced Processing and Manufacturing Technologies for Structural and Multifunctional Materials IV, CESP Volume 31, Issue 8 (includes papers from Symposium 8)
- Advanced Materials for Sustainable Developments, CESP Volume 31, Issue 9 (includes papers from Symposia 6, 10, and 11)
- Strategic Materials and Computational Design, CESP Volume 31, Issue 10 (includes papers from Focused Sessions 1, 3 and 4)

The organization of the Daytona Beach meeting and the publication of these proceedings were possible thanks to the professional staff of ACerS and the tireless dedication of many ECD members. We would especially like to express our sincere thanks to the symposia organizers, session chairs, presenters and conference attendees, for their efforts and enthusiastic participation in the vibrant and cutting-edge conference.


Sanjay Mathur and Tatsuki Ohji, Volume Editors
July 2010
Thermal and Environmental Barrier Coatings
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KINETICS AND MECHANISM OF OXIDATION OF THE REINFORCED CARBON/CARBON ON THE SPACE SHUTTLE ORBITER

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ABSTRACT

Reinforced carbon/carbon (RCC) protects the Space Shuttle Orbiter wing leading edge and nose cap from the heat of re-entry. The oxidation protection system is based on a SiC conversion coating. In this paper, fundamental laboratory oxidation studies from 600-1200°C on RCC fabric, fabric and matrix, and SiC-protected carbon/carbon are discussed. Although conducted under laboratory conditions, these studies reproduce the morphologies observed under flight conditions. Oxidation below ~900°C is reaction-controlled and is characterized by preferential attack of the matrix and thinning of the fibers. Further microscopy reveals that oxidation begins with preferential attack into the grooves of the fibers. At ~900°C, there is a transition to diffusion-controlled oxidation. This is characterized by more localized attack near the surface of the carbon/carbon. For SiC-coated RCC, cavities form at the base of cracks in the SiC. This morphology lends itself to a two-step diffusion model for carbon oxidation. Fluxes are considered in both the SiC channel and growing cavity. Experiments show good agreement with the model predictions. These studies show the criticality of a stable coating system with filled cracks to protect RCC.

INTRODUCTION

A unique series of design features and materials protect the Space Shuttle Orbiter from the heat of re-entry, which leads to temperatures in excess of 2800°F (1538°C) for several minutes in certain locations. The hottest parts of the Orbiter are the wing leading edge and nose cap. These are fabricated of a reinforced carbon/carbon (RCC) material which has performed remarkably well in nearly thirty years of service and well over 100 flights. Fig. 1 shows the location of the RCC panels on the Orbiter.

RCC was developed well over thirty years ago by Vought Aircraft (now Lockheed Missiles and Fire Control). A diagram of this material is shown in Fig. 2 and an actual cross section is shown in Figs. 3(a) and (b). It is composed of a two-dimensional lay-up of carbon fabric. The fibers in this cloth are derived from a rayon precursor and they are about 10 μm in diameter with a fairly uniform microstructure. Fig. 3(b) shows that the outer edges of the fibers exhibit crenulations or grooves, which are characteristic of wet-spun fibers.
The two dimensional lay-up of cloth is repeatedly infiltrated with a liquid carbon precursors to fill porosity. However, it should be noted that not all voids are filled and, in fact, some of the additional processing steps require interconnected porosity. Fig. 3(a) shows a polished cross-section of RCC. Note the extensive porosity in the carbon/carbon substrate. This is due to incomplete compaction and shrinkage cracks on cooling.

Oxidation protection is, of course, a critical issue for RCC. The primary oxygen barrier is a conversion coating of SiC. Due to the thermal expansion mismatch the SiC forms through-thickness cracks upon cooling from the processing temperature of ~1650°C. The entire piece is vacuum infiltrated with TEOS (tetra-ethyl orthosilicate), which decomposes on a mild heat treatment to SiO₂. Then the faces are coated with a glass sealant. This sodium silicate glass becomes fluid at high temperatures and effectively seals the cracks in the SiC. The sodium silicate contains SiC grit and chopped SiC fibers which act as a filler and limit frothing. The oxidation protection system is illustrated in the schematic in Fig. 2 and the actual cross-section in Fig. 3(a).

The glass system is remarkably effective and post-examination of specimens exposed to hot gases, when the glass is molten, show little oxidation. Nonetheless, there are conditions when the oxidation protection system is not operative. At low temperatures, when the glass is not fluid, cracks and fissures in the SiC coating can lead to oxidation of the carbon/carbon. At higher temperatures, the glass becomes depleted either due to vaporization or shear forces, and oxidation may occur. Vaporization, primarily as loss of the sodium component, becomes appreciable at temperatures greater than ~1200°C. The outer coating of sodium silicate has been on a regular refurbishment schedule to prevent this, but some oxidation has been observed on panels as the glass is depleted.

For this reason, RCC oxidation has been studied by several investigators. These studies have been conducted in arc-jets, which most accurately reproduce the re-entry environment in regard to pressures, temperature, velocities and dissociated oxygen. However, arc-jet tests are complex and expensive and it is difficult to accurately control all variables. We have found that many of the morphological features observed on mission-exposed RCC can be reproduced in simple laboratory furnace tests. These laboratory tests involve diatomic oxygen at low flow rates and only can capture the temperature component of re-entry. Nonetheless, a good deal can be learned from these basic studies.

The reaction of carbon and oxygen at elevated temperatures is one of the most studied topics in high temperature oxidation. The key steps in oxidation are given below.
1. Diffusion of oxygen to the carbon surface.
2. Chemical reaction at the surface.
3. Diffusion of the products CO and/or CO₂ away from the surface.

In general, carbon oxidation exhibits a low temperature (~400-900°C) region where the overall rate is controlled by the chemical reaction. In reaction-controlled oxidation, the rates are highly dependent on temperature and the type of carbon. Morphologies in this region indicate selective attack of specific microstructural features. At temperatures above ~900°C, the process is controlled by diffusion of oxygen to the sample or diffusion of the products away from the sample. In diffusion-controlled oxidation, the reaction rates exhibit only a weak dependence on temperature. Generally a more uniform reaction front is expected, as the rate of oxidation does not depend on the particular form of carbon in a localized region.
In this paper, the kinetics and mechanisms of RCC oxidation are reviewed. We discuss RCC with and without a SiC coating. The transition from reaction-control to diffusion-control is discussed both in terms of the Arrhenius plot and some important morphological changes. Additionally, a model for diffusion-controlled reaction is discussed.

EXPERIMENTAL

The starting material was the same type of RCC used on the Orbiter. Oxidation of fibers in the form of cloth and oxidation of the composite material with and without a conversion coating of SiC was studied. The RCC with a SiC coating was in the form of 1.91 cm diameter discs with all sides coated.

Fibers in the form of a cloth were oxidized in a thermogravimetric apparatus (TGA). The TGA used consisted of a vertical tube furnace with a 5 cm hot zone and microbalance. Cloth samples of ~0.30 g were placed in an alumina cup with slots cut in the bottom for gas flow. The carbon/carbon composites were prepared as cubes with ~0.5 cm sides and placed on an alumina platform with slots in the bottom. Tests were conducted in oxygen or air at a flow rate of 100 cc/min. Weight change and temperature data was collected with an automated collection system. Rates were taken as the instantaneous slope at 50% consumption, according to convention for carbon materials. Oxidation rates were measured every 100 degrees between 500 and 1200°C.

Fibers and the actual carbon/carbon composite were mounted in epoxy and polished with diamond pastes for optical and electron-optical examination of both the as-fabricated and post-oxidation samples. Scanning electron microscopy was done with a Hitachi S4700 Cold Field Emission Scanning Electron Microscope (FE-SEM), equipped with an x-ray energy dispersive spectrometer (XEDS) for elemental analysis. A thin carbon film was evaporated onto the surface of mounted and polished samples to provide conductivity for the FE-SEM examination.

For the studies relating to the diffusion model, two sets of experiments were performed. The first set of experiments were done with 1.9 cm diameter disc of RCC with a SiC coating on all sides and a TEOS treatment. Slots of 0.53 and 1.02 mm width were made to the SiC/carbon-carbon interface. Oxidation treatments were done at 1200°C in a box furnace with static laboratory air. Oxidation damage was assessed by weight changes and optical microscopy of cross-sections. Image analysis software (Foveapro, Reindeer Graphics) was used to measure the cross sectional area of the oxidation cavity. The areas were approximated as a semi-circle and the radii extracted.

The second set of experiments were done with 1.9 cm diameter disc of RCC with a SiC coating on all sides and a TEOS treatment. Slots were not machined in these and oxidation occurred only through the natural craze cracks. The crack pattern was clearly revealed in a specimen by polishing a few hundred microns off the surface, as shown in Figs. 4(a) and (b). From this photo as well as cross sectional views, crack parameters such as crack length/unit area, crack width, and coating thickness were measured and used in the model. The specimens with natural craze cracks were oxidized in the TGA.
RESULTS AND DISCUSSION

A typical TGA plot is shown in Fig. 5(a) for the fibers as cloth at 900°C in air. In two hours the fibers were completely consumed. A typical TGA plot for the fibers and matrix material at 600°C in air is shown in Fig. 5(b) and is significantly different. It takes nearly fifty hours to consume the fiber and matrix at this lower temperature. The rapid weight loss at the beginning of the test is likely due to matrix oxidation, which often oxidizes faster than the fibers as it is less crystalline. This is consistent with microstructural observations.

Fig. 6 is an Arrhenius plot of the oxidation rates of the fibers. These data show a characteristic change from a strongly temperature-dependent region below ~800°C to a weakly temperature-dependent region above ~800°C. The lower temperature region is thus attributed to reaction-control, whereas the higher temperature region is attributed to diffusion-control. Fig. 6 shows rates measured in air and oxygen. While there is not enough data to obtain an oxygen pressure dependence, the rates definitely decrease with oxygen pressure. Also note that the results of Halbig for a T-300 carbon fiber are similar in the diffusion control region, but differ in the reaction-control region. The T-300 carbon fibers have outer layers of porosity which leads to diffusion control at lower temperatures.

Reaction-control leads to a distinct morphology of attack. Fig. 7 is a micrograph of the fibers after 6.5 hrs at 600°C in air. Note the preferential attack in the form of fissures into the fibers. These fissures are not present in the as-fabricated material and are formed during oxidation. Attack is also observed in the form of thinning or denuding of the fiber diameter, leading to the smaller diameter fibers observed in Fig. 8(a).

Figs. 8(a) and (b) illustrate the reaction-controlled and diffusion-controlled oxidation in the RCC fibers and matrix, respectively. Note the reaction-controlled microstructure indicates oxidation throughout and thinner fibers. However the diffusion-controlled microstructure indicates a dense center, with oxidative attack near the outer edges. This is consistent with the observation of Halbig and Cawley on oxidized carbon fiber/SiC matrix composites. Generally, the Arrhenius behavior and reaction-control to diffusion-control transition of RCC fibers and matrix material is very similar to the fibers alone. The major difference is the matrix tends to oxidize faster than the fibers, as shown in Fig. 5(b). However, as the matrix is heated to higher temperatures and graphitizes, it is likely that the matrix and fiber would begin to show similar oxidation rates.

For SiC-protected RCC, the behavior is more complex. The transition from reaction-control to diffusion-control is easiest to observe microstructurally, as shown in the sequence in Fig. 9. In this sequence a small slot has been cut in the SiC coating to the carbon/carbon substrate to provide a clear path for oxygen to the carbon/carbon substrate. Note that at the lowest temperatures, there is only a small region around the slot which is oxidized, as evidenced by the thinner fibers in this region. As temperature is increased, a hemispherical cavity (in two dimensions) or half-cylinder trough (in three dimensions) forms. This type of attack is characteristic of diffusion-control oxidation where attack is uniform in all directions. Further, the geometry of such attack allows it to be readily modeled. These models have been discussed elsewhere, but will be briefly summarized here.

In low oxygen potentials, carbon oxidation leads to CO(g). However, CO(g) and O₂(g) are thermodynamically incompatible. They will react to form the more thermochemically stable CO₂(g). For this reason, oxidation of carbon is generally treated in two steps:
Kinetics and Mechanism of Oxidation of the RCC on the Space Shuttle

At the carbon/gas interface: \[ C(s) + CO_2(g) = 2 CO(g) \] \[ 1 \]

At a distance away from the carbon/gas interface: \[ CO(g) + \frac{1}{2} O_2(g) = CO_2(g) \] \[ 2 \]

The net reaction is the oxidation of C to CO(g), but separation to these two steps avoids the CO/O_2 incompatibility problem. Further, combustion studies of carbon show this secondary reaction front is located at a distance away from the solid surface.\[ 18 \]

There are several studies in the literature of carbon oxidation through channels (slots or cracks) in an inert matrix.\[ 5-13 \] The equations for this type of oxidation are well established and have been presented by these investigators. In this treatment, we include diffusion not only through the SiC channel, but also through the growing oxidation cavity. A schematic of this process is shown in Fig. 10.

As suggested by the microstructure, the diffusion equations for the channel are in rectangular coordinates and the growing cavity in polar coordinates. The equations for the flux in the channel are written as:

\[ J_i = D_i^{eff} \left( \frac{\partial c_i}{\partial x} \right) + v_i^{conv} c_i \] \[ 3 \]

Here \( J_i \) is the flux of species \( i \), \( D_i^{eff} \) is the effective diffusion coefficient of the species \( i \), \( c_i \) is the concentration of species \( i \), \( x \) is the distance along the channel, and \( v_i^{conv} \) is the average velocity of species \( i \). The first term in this expression is the diffusive flux and the second term is the convective flux. The convective flux can be simplified since:

\[ v_i^{conv} = \frac{\sum c_i v_i}{\sum c_i} = \frac{\sum J_i}{c_T} \] \[ 4 \]

Here \( c_T \) is the total of the concentration of species \( i \). The boundary conditions are as follows:

At the base of the channel: \( x = 0 \) : \[ c_{CO} = c_{CO}^0 \quad c_{CO_2} = c_{CO_2}^0 \]

At the site of reaction [2]: \( x = x_f \) : \[ c_{CO} = c_{CO}^* \quad c_{O_2} = c_{CO} = 0 \] \[ 5 \]

At the mouth of the channel: \( x = L \) : \[ c_{O_2} = c_{O_2}^L \quad c_{CO_2} = 0 \]

As discussed, these equations have been solved analytically by several investigators.\[ 7, 9, 19-24 \] The first step is to derive an expression for \( x_f/L \), where \( L \) is the thickness of the coating. Then an expression for the flux of CO_2 is developed, which relates to the carbon consumption.

The oxidation model is further extended by adding the fluxes in the growing cavity. As noted, these are best written in polar coordinates.
Kinetics and Mechanism of Oxidation of the RCC on the Space Shuttle

\[ J_{CO_2}^r A' = -D_{CO_2} A' \left( \frac{\partial c_{CO_2}}{\partial r} \right) - \frac{A' c_{CO_2} J_{CO_2}^r}{c_r} \]  

[6]

Here, \( J_{CO_2}^r \) is the flux of \( CO_2 \) in the growing 'trough' (see Fig. 8), \( A' \) is the area of exposed carbon for oxidation, and \( r \) is the radius of the trough. The flux of \( CO_2 \) at the base of the channel is then equated to the flux of \( CO_2 \) entering the trough. The resultant equation is solved for the concentration of \( CO_2 \) at \( r_1 \) (radius at time 0), \( c_{CO_2}^0 \), and this quantity is then inserted into the integrated form of equation [6].

Assuming a reaction probability of one, the flux of \( CO_2 \) can be related to both a radius of the growing trough and a weight loss. It is not possible to solve for trough radius or weight loss as a function of time. Nonetheless, the reverse can be done and the following equations are used to generate oxidation kinetics. The time, \( t \), as function of trough radius, \( r_2 \), is given by:

\[ t = \frac{M_{CO_2}}{M_c \ D_{CO_2} c_{CO_2}} \left[ \frac{r_2^2 \ln(r_2)}{4} - \frac{r_2^2}{4} \ln r_1 + \frac{r_2^2}{2} \left( \frac{\pi x_f (c_T + c_{CO_2}^*)}{r_1 c_T} \right) + \frac{r_2^2}{4} \right] \]

[7]

The time, \( t \), as a function of weight loss, \( W \), is given by:

\[ t = \frac{M_{CO_2}}{M_c \ D_{CO_2} c_{CO_2}^*} \left[ \frac{\left( \frac{2W}{\pi pl} + r_1 \right)^2}{2} \ln \left( \frac{2W}{\pi pl} + r_1 \right) - \frac{\left( \frac{2W}{\pi pl} + r_1 \right)^2}{4} \right] \]

[8]

Here, \( M_i \) is the molecular weight of species \( i \), \( D_i \) is the diffusivity of species \( i \), \( c_{CO_2}^* \) is the concentration of \( CO_2 \) at position \( x_f \), \( \rho \) is the density of carbon/carbon, \( l \) is the crack length, \( c_T \) is the total concentration of gaseous species in the crack, and \( r_1 \) is shown in Fig. 9(c). Although equation [8] is
complex, it was found that the linear terms dominate and a linear weight loss term can be derived for comparison to experiment.

An important consideration is the change of the channel geometry with temperature. Two possible changes can occur. The craze cracks should ideally close as temperature increases. Clearly this does not occur, as oxidation is still observed. For the purposes of this approximation, the room temperature crack width is used. The second consideration is crack wall oxidation. Electron microscope observations indicated only very thin oxide films (<0.5 μm) are formed and most of the oxidation is internal oxidation of the porous SiC coating. For this reason, oxidation crack width changes due to oxidation were neglected.

As discussed in the experimental section, two types of experiments were done to test the model. First slots were machined and radii measured from cross-sections, similar to Fig. 9(d). Fig. 11 compares experimentally measured radii from oxidation exposures to the model for two different slot widths. The solid line shows the model for diffusion only in the slot, ignoring the growing oxidation void. The dashed line shows the model for the coupled equations of diffusion in the slot and the void (equation [7]), and shows good agreement with the experimental data.

The second type of experiment was performed with the RCC being coated on all sides with SiC and oxidation through the naturally occurring craze cracks was measured. Specimens were characterized as described in the experimental section and oxidation exposures were done in a TGA with flowing air. These continuous weight-change measurements exhibited a weight gain for the first 1 hr or so of the oxidation run and then a smooth linear weight-loss. This weight-loss rate was determined and reported in Table I.

The results from the model are shown in Table I. Neither the craze cracks or the resultant oxidation cavities (Fig. 12) formed the uniform geometries observed with the machined cracks. A 'tortuosity' factor was not used to account for this non-ideality. Nonetheless, the agreement between the model and the experiments is quite reasonable suggesting the deviations from non-ideality are not great and/or tend offset each other.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Area of Carbon exposed craze cracks, mm²</th>
<th>Measured weight loss mg/mm²-hr</th>
<th>Calculated weight loss mg/mm²-hr</th>
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</thead>
<tbody>
<tr>
<td>1000</td>
<td>3.60 ± 0.923</td>
<td>26 ± 7</td>
<td>14.7</td>
</tr>
<tr>
<td>1100</td>
<td>3.96 ± 0.63</td>
<td>21 ± 6</td>
<td>13.6</td>
</tr>
<tr>
<td>1200</td>
<td>3.99 ± 0.132</td>
<td>30 ± 8</td>
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<tr>
<td>1300</td>
<td>3.97 ± 0.019</td>
<td>41 ± 9</td>
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</tr>
</tbody>
</table>

SUMMARY AND CONCLUSIONS

Reinforced carbon/carbon has been successfully used on the Orbiter wing leading edge and nose cap for well over 100 missions. The structure of this remarkable material has been discussed. Oxidation is a primary concern for RCC as well as for other carbon/carbon structural materials. Basic laboratory studies on oxidation of the rayon-derived carbon fibers, carbon fibers and matrix, and SiC protected carbon/carbon have been discussed. Characteristic microstructures are shown for the reaction-controlled and diffusion-controlled regions. In the reaction-controlled region, oxidation...