### Formation of Solid Intermediates on Particles

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Oxidation of solid particles is a common process in nature and technology. Metal catalyst particles tend to form *solid* oxidized species that often grow as films on the unreacted metal core and propagate into the core, accompanied by *particle expansion* which is typically not being accounted for. This expansion can be substantial for nanoparticles.

Carbon particles ultimately form *volatile* species such as CO and CO2 upon oxidation - the typical coal combustion process and also carbon aerosol (soot) ageing and weathering in the atmosphere, accompanied by *decrease of the particle size* until all carbon is converted. This process is analog to fluorination of uranium oxide, which is converted into gaseous UF6.

We report here observations made during the oxidation of carbon and fluorination of uranium oxide, particularly the preliminary particle expansion, which suggests that solid intermediate species of materials are formed which have been hitherto known only as volatiles. The chemical and structural nature of these intermediates is not yet fully understood. We try to mathematically model the film growth to the extent that we are aware of the physical properties.

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Carbon particles ultimately form *volatile* species such as CO and $CO_2$ upon oxidation - the typical coal combustion process and also carbon aerosol (soot) ageing and weathering in the atmosphere, accompanied by *decrease of the particle size* until all carbon is converted. This process is analog to fluorination of uranium oxide, which is converted into gaseous $UF_6$.

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## Model System: Glassy Carbon

Closed voids in highly porous glassy carbon (GC) become opened and connected by oxidation, forming a film with open porosity on top of the carbon core. Superimposed to the film growth is the depletion of the film by combustion - the carbon sample size decreases during oxidation and ultimately vanishes [1,2].



$P(t) = L - a \cdot t$ ; $D(t) = P(t) - Q(t) =$ film thickness
$a \sim$ reaction rate ; $b \sim$ diffusion constant

$$(a + \dot{D}) \cdot D - b = 0$$
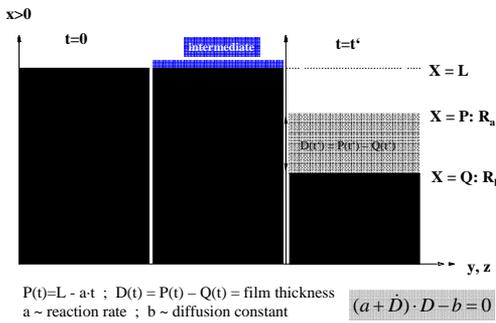
**Figure 1**: Schematic of glassy carbon *disk* (black) exposed to oxygen at high temperatures. Less bound carbon atoms are preferentially oxidized, making it a **porous film (grey)** on the **unreacted core (black)**. By diffusion, oxygen propagates through the film to the film/core interface. At the same time, further oxidation at the film/gas boundary burns off the film, thinning the disk. The **intermediate film on top (blue)** indicates sample expansion due to solid intermediates. This intermediate, very thin film has escaped attention.

The film growth for the above system has an **exact analytical solution** for the above equation with *burn-off constant a* and *diffusion constant b* [3]:

$$D(t) = P(t) - Q(t) = \frac{b}{a}\left(1 + W\left(-\exp\left(-1 - \frac{a^2 t}{b}\right)\right)\right)$$

$$A_{(g)} + b \cdot B_{(s)} \xrightarrow{k_1} c \cdot C_{(s)}$$

$$A_{(g)} + c' \cdot C_{(s)} \xrightarrow{k_2} gas \quad products$$
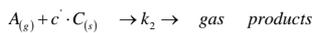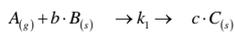
The intermediate is only noticed as a small sample expansion (1 micron) during very early stage of activation, prior to any substantial burn-off. Intermediate formation goes along with an ultra-high roughness on the material, as evidenced by small-angle x-ray scattering (SAXS, Fig. 3). One minute of oxidation in air at 450°C forms a thin ~ 1 micron layer on the smooth glassy carbon with a huge x-ray scattering contrast.



SAXS data recorded at
JUSIFA Beamline
HASYLAB Hamburg Synchrotron
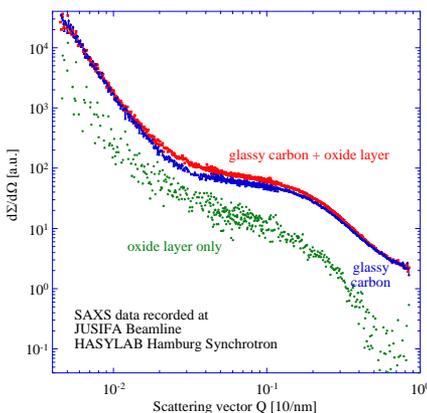
**Figure 2**: SAXS of non-oxidized (blue) and slightly, one minute surface-oxidized (red) glassy carbon. The difference of both curves (green) is attributed to the ~ 1 micron intermediate film, where no burn-off has taken place yet, and ranges about 3000 $m^2/g$ !
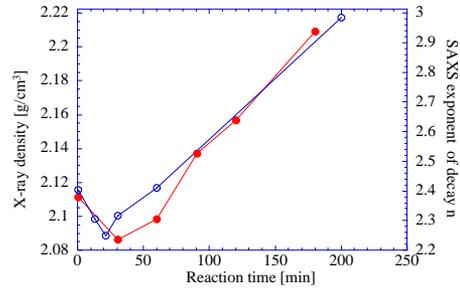


**Figure 3**: X-ray density and SAXS exponent of decay have a minimum after brief oxidation of GC, indicating formation of a highly porous, open structure that coincides with particle expansion [4].
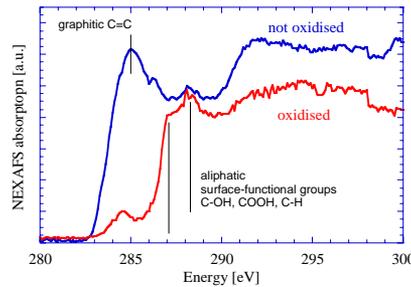


**Figure 4**: Surface sensitive carbon (1s) x-ray absorption spectrum shows evolution of surface functional groups on glassy carbon as a result of oxidation [5].

## Intermediates on Soot by Weathering
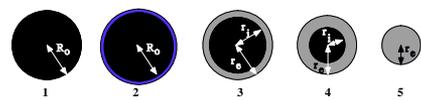


**Figure 5**: Variation of the unreacted core thickness $r_i$ for particles with spherical geometry. The **Blue ring** indicates stage (2) of thickness maximum due to intermediate formation.
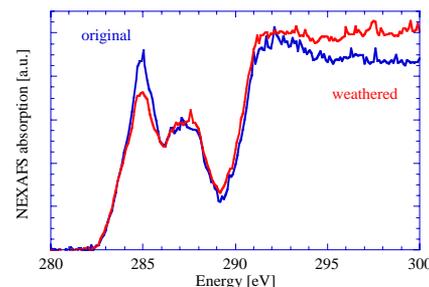


**Figure 6**: Surface sensitive carbon (1s) x-ray absorption shows relative enhancement of surface functional group intensity on diesel soot during weathering, in analogy to glassy carbon oxidation [5].

## Fluorination of Uranium Oxide
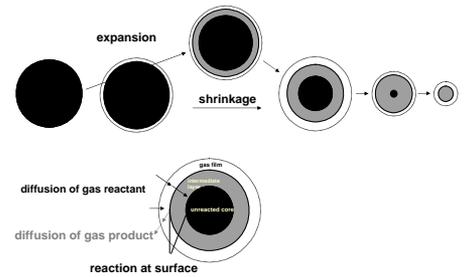


**Figure 7**: Schematic of the reaction model for $UO_2$ for expanding, then shrinking particle with unreacted shrinking core.

The specific reaction scenario is the formation of a solid intermediate $UO_2F_2$ by fluorination of $UO_2$, and the subsequent formation of gaseous products upon further fluorination [6]:

$$F_{2(g)} + UO_{2(s)} \xrightarrow{k_1} UO_2F_{2(s)}$$

$$F_{2(g)} + \frac{1}{2} \cdot UO_2F_2 \xrightarrow{k_2} \frac{1}{2} \cdot UF_{6(g)} + \frac{1}{2} \cdot O_{2(g)}$$
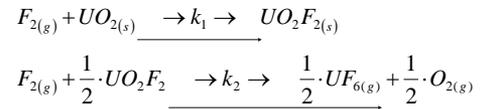
An analytical solution for the film thickness on samples with spherical geometry (Figs. 5, 7) could not yet be derived. Fig. 8, left, presents numerical results on film growth without intermediate formation. Formation of intermediates and quantitative treatment has not yet been addressed in the literature. Figure 8, right, includes sample expansion by intermediate formation on top of particle.
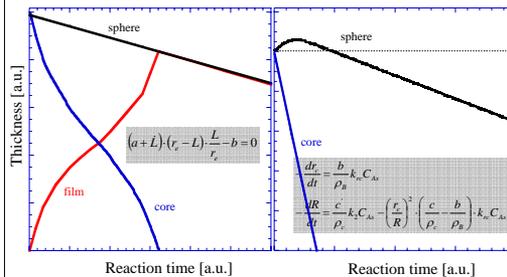


**Figure 8**: Left – numerically obtained thicknesses for particle, core and film as a function of reaction time, representative of Figure 5 for carbon. Right – numerically obtained changes of sphere and core thickness during fluorination of $UO_2$.

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## Acknowledgment