

ON THE EVOLUTION OF OXYGEN SURFACE COMPLEX OF A SINGLE CHAR PARTICLE DURING OXIDATION

Xuefeng Zhang and Ezra Bar-Ziv
 Department of Mechanical Engineering
 Ben-Gurion University of Negev, Beer-Sheva, Israel

Introduction

Extensive efforts have been made to investigate surface kinetics in char oxidation. It is well accepted that oxidation of char proceeds through carbon sites that adsorb oxygen and desorb carbon oxides. TGA have been extensively utilized to study char adsorption and desorption kinetics by oxygen chemisorption. Transient kinetics (TK) is also being used, where the reactant was replaced by an inert gas during oxidation then oxygen complexes were desorbed, at the reaction temperature or subjected to a temperature programmed desorption (TPD) [1,2]. The limitation in a TGA is imposed from the speed at which gases can be exchanged (order of minutes). In this communication, a methodology to study surface kinetics of a single particle suspended in an electrodynamic chamber (EDC) [3] is presented. Single synthetic (Spherocarb) particles were oxidized to a certain burnoff, quenched rapidly, then the reactant was replaced by an inert gas to desorb the surface complexes which were frozen from oxidation.

particle at the center of the EDC and measures the 3-D forces on the particle.

For a suspended particle without laser heating, particle weight is $qE=mg$ (q is charge, E is electric field strength, m is mass and g is gravitational acceleration). Since q is constant during oxidation [3], the particle instant mass is,

$$m(t)/m_0 = V(t)/V_0 \quad (1)$$

m_0 is particle initial mass, V is voltage and t is time.

Results

Experiments were conducted with Spherocarb particles of initial diameter of 200 μm and density of 800 kg/m^3 (about 60% porosity).

First, the particle was heated to 800 K in pure N_2 to clean the particle surface (desorption of initial oxide complexes), see Fig. 2. The particle lost 16% of its initial mass in 1 hr, then no mass loss was observed any more. At the end of the cleaning stage the particle was cooled to ambient temperature and nitrogen was replaced by pure oxygen. No mass change was observed even after one hour, indicating no adsorption of oxygen at room temperature. The particle was then heated (in oxygen) to 800 K and let to be oxidized for a while with a typical conversion rate of $7 \cdot 10^{-4}$ g/g-s, see Fig. 3.

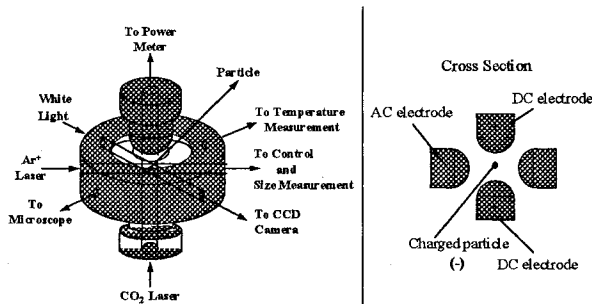


Figure 1. Exploded overview of the electrodynamic chamber and its cross section.

Experimental

Experiments were conducted in an EDC. A schematic description of the EDC, with its various operation and diagnostic systems, is presented in Figure 1. The EDC consists three pairs of DC electrodes along x, y and z to balance the 3-D forces imposed on the particle. The AC ring electrode provides dynamic stability to the suspended particle. An essential part of the EDC is a fast 3-D position controller [4]. The controller maintains the

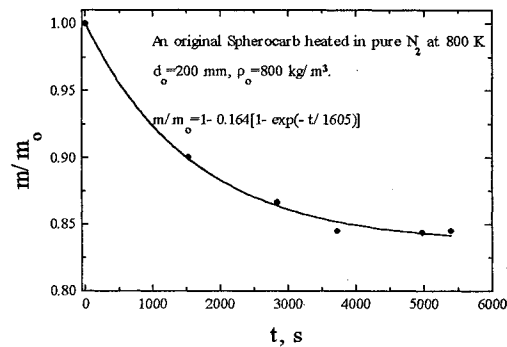


Figure 2. Mass versus time of a Spherocarb particle heated in nitrogen at 800 K.

After a predetermined burnout extent, the particle was cooled back to ambient temperature within 0.01 s and oxygen was replaced by nitrogen. Particle (in nitrogen) was then heated to 800 K and mass history was recorded, see Fig. 4. Mass loss (presumably carbon oxide -- probably CO and not CO₂) of about 2.2% of initial mass.

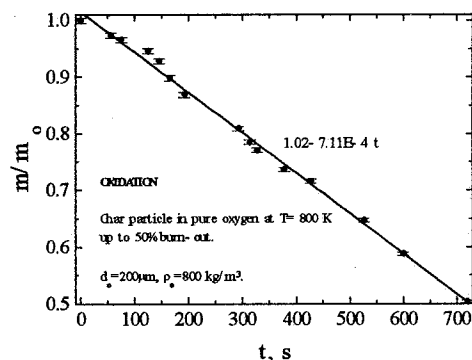


Figure 3. Mass versus time, from end of the previous stage (Fig. 2), after particle was cooled to ambient temperature and nitrogen was replaced by pure oxygen.

After the reaction and desorption process, at 50% burnout, the particle was subjected to another 5% burn-out at the same temperature, mass loss of 1.5% of initial mass was found in the subsequent heating in N₂. This is about 3/4 of the previous desorption.

The preliminary experiments suggest that the main advantage by using a suspended particle is the fast cooling process that enables quenching oxidation within 0.01 s, then subsequent gas exchange can be operated when the particle is cool. This allows to freeze surface complex from oxidation for subsequent desorption analysis. Whereas in TGA experiments, oxidation is quenched by switching oxygen environment to inert gas when the particle is hot. The long time of gas switching process (on the order of minutes) leads to question on its ability to freeze particle surface complex from precedent oxidation since oxidation can continue during gas exchange process.

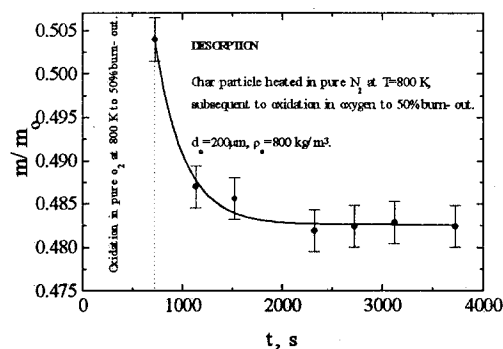


Figure 4. Mass loss versus time, after a predetermined burnout extent, the particle was cooled back to ambient temperature and oxygen was replaced by nitrogen.

Conclusion

As one can see, the suspended particle experiment opens new paths in the elucidation of the adsorption-desorption mechanisms and enables the uncoupling of the two processes by operating alternately with adsorbed and non-adsorbed gases (O₂ and N₂ in our case). The fast quenching rate of the suspended particle experiments allows directly freeze particle surface complex from oxidation. Hence, new insight into particle surface kinetics and oxidation mechanism will be gained.

Reference

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