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Oxidation protection of C/C–SiC composites by an electrophoretically deposited mullite precursor: Cyclic thermogravimetric analysis

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Abstract

Sufficiently thick and homogeneous layers which transform into mullite at $T \geq 1000\,^\circ\mathrm{C}$ were synthesized by means of sol–gel technology and electrophoretically deposited onto the surface of C/C–Si–SiC composites. The protectiveness of the deposited mullite layers was isothermally tested in air in the temperature range $1200 \leq T \leq 1550\,^\circ\mathrm{C}$ for up to 200 h. At temperatures above 1600 °C, the protectiveness of the deposited layer is reduced due to the existence of a liquid phase and the formation of CO bubbles above the cracks in the SiC layer. In order to prolong the protectiveness of our mullite layers at higher temperatures an additional layer from a suspension of mullite precursor with 5 wt.% of Al_2O_3 powder was deposited. The protectiveness of the obtained mullite and mullite/Al_2O_3 multilayer systems were also tested under cyclic conditions. These experiments yielded encouraging results, which will have to be confirmed at higher temperatures.

Keywords: Mullite; Composites; Sol–Gel Synthesis; Electrophoretic deposition

1. Introduction

The starting industrial material was a SiC coated carbon-reinforced carbon composite (C/C) (Schunk Kohlenstofftechnik GmbH, Heuchelheim, Germany) in the form of thin slabs with average dimensions 20 mm × 20 mm × 2 mm.[1,2] The SiC layer was chemically vapour deposited after the C/C substrate had first been capillary infiltrated with liquid silicon. As both processes take place at high temperatures many cracks develop in the SiC layer after cooling down to room temperature. These cracks are generally closed after prolonged oxidation above 1100 °C. The resulting protective SiO_2 layer is a suitable diffusion barrier for oxygen but it degrades during prolonged service beyond 1300 °C.

Mullite was chosen as an outer refractory oxide layer which provides an additional oxidation protection for C/C–Si–SiC composites.[3,4] Mullite is the only stable binary phase of the system Al_2O_3–SiO_2 existing at ambient conditions and has the following composition range: $x\mathrm{Al_2O_3}\cdot\mathrm{SiO_2}$, $1.5 \leq x \leq 2.0$.

The main advantages of mullite as a protective system are: a low thermal expansion coefficient matching that of the underlying SiC layer, a high melting point and a particularly low oxygen diffusion coefficient.

2. Experimental

Reagent grade chemicals for the synthesis of the mullite precursors were the corresponding alkoxides of Si and Al together with isopropanol as the solvent. Through a variation of the synthesis parameters (amount of water added for hydrolysis, pH of water, concentration of alkoxide and concentration of β-diketone) different mullite precursors were obtained. These precursors were further characterized regarding their stability (by means of Electrokinetic Sonic Analysis – ESA measurements) and suitability for electrophoretic deposition (EPD). These measurements showed that the synthesis of a mullite precursor suitable for EPD is possible under the conditions described in our previous paper.[2]

In order to prolong the oxidation protection of the mullite layers under cyclic thermal conditions additional suspensions based on the obtained mullite precursor sol were prepared. A

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nanoscale Al_2O_3 powder (Degussa GmbH, Germany) with an average particle size of 13 nm was added which should serve as a reservoir for mullite formation from the growing SiO_2 layer during oxidation. Stable suspensions of mullite precursor sol and Al_2O_3 powder were obtained for concentrations of up to 5 wt.% of Al_2O_3. Upon dispersion of Al_2O_3 powder in the mullite precursor sol it was observed that the stability of the suspension increases with the amount of Al_2O_3 powder added, due to the fact that Al_2O_3 particles are positively charged in isopropanol.

For the preparation of protective coatings on the surface of C/C–Si–SiC composites electrophoretic deposition was used.[1,2] EPD was performed cathodically varying the voltage and the duration of the deposition. The best performance of the deposited layer regarding the adhesion to the C/C–Si–SiC substrate was achieved at 15 V/cm and 15 and 30 s deposition time.

For the given conditions, it was possible to produce mullite layers with thicknesses of 7.5 and 13 μm, respectively. The mullite layers were deposited in five EPD cycles from MP sol without added Al_2O_3. After each cycle the green layers were sintered under Ar at 1300 °C for 2 h. The heating and cooling rates were 2 °C/min. Additional deposition of MP + 5 wt.% Al_2O_3 at 15 V/cm and 15 s leads to an increase of the mullite layer thickness by approximately 3 μm.

The protectiveness of the electrophoretically deposited mullite layers against oxidation was already investigated by means of isothermal thermogravimetric analysis in air in the temperature range $1200 \leq T \leq 1600$ °C.[1,2] As the protective layer systems are even more attractive if they offer an oxidation protection under cyclic conditions it was necessary to test the protectiveness of our mullite layers under cyclic conditions. These experiments were performed as follows:

The samples (size 20 mm × 20 mm × 2 mm, five times coated with a mullite layer and after an additional sixth deposition from mullite/Al_2O_3 suspension, average mass m = 1.8 g) were cooled rapidly from the operating temperature at 1500 or 1550 °C by pulling it out from the furnace within 100 s. For the next 8.3 min, the samples remained at room temperature and after this period there were again brought into the furnace within 100 s (Fig. 1) for a duration of approximately 1 h. The average heating and cooling rate was 15 °C/s and thermogravimetric experiments were performed in air.

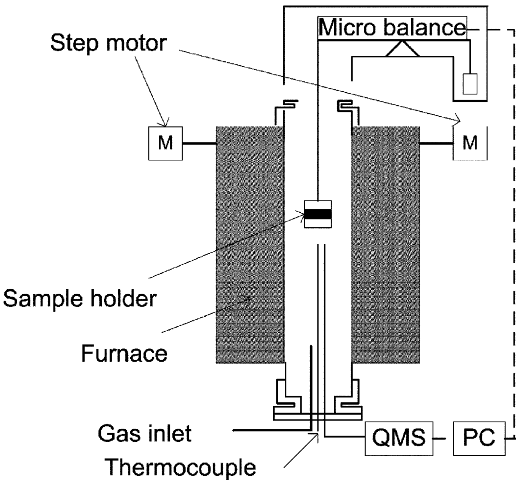

Fig. 1. Experimental set-up for cyclic thermogravimetric experiments. QMS: Quadrupol mass spectrometer for gas analysis between 1 and 1000 mbar.

For every temperature, three to six samples were tested (average duration of the experiments was about 13 days without burn-out of the sample).

3. Results and discussion

In the following, the typical cyclic oxidation curves for the samples at 1500 and 1550 °C are presented (Figs. 2 and 3). In Figs. 2a and 3a, one can see that the cycles were repeated in intervals of 2–3 days. For substrates which sustained more than 200 h at oxidation temperature (ca. 80% of coated substrates) the cycles were repeated every hour (Figs. 2b and 3b) in order to see if the samples could resist to such severe conditions. Our experiments showed that all samples withstood at least for 4-12 cycles. A mass loss of about 2 mg per cycle was common to all cycles. Up to 1500 °C, there was no difference observed in the oxidation kinetics under cyclic conditions for samples, which were coated five times with mullite and samples, which were additionally coated from a suspension of mullite and Al_2O_3. At 1550 °C, an improvement in oxidation protection was observed for samples coated with an additional mullite and Al_2O_3 layer whereas the samples coated only with mullite started burning out after the second cycle.

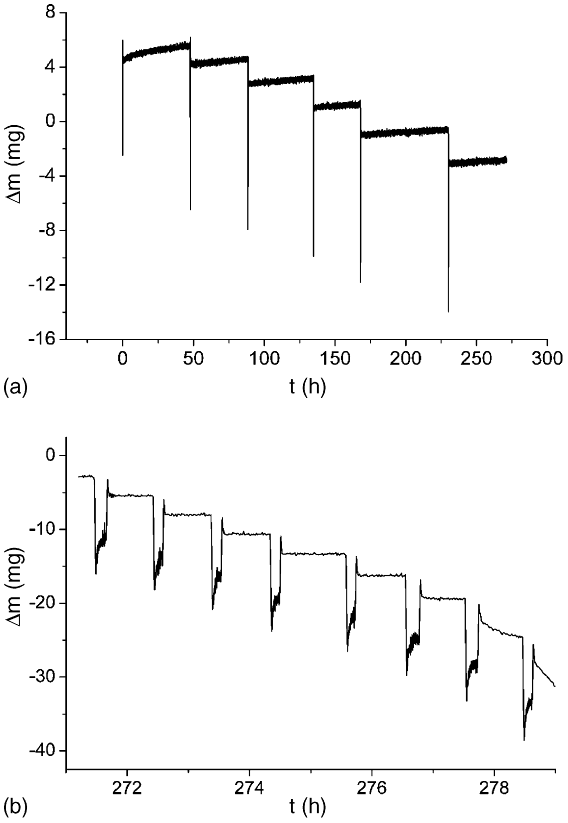

Fig. 2. Cyclic oxidation curves for samples electrophoretically coated with mullite and an additional mullite/Al_2O_3 layer at 1500 °C: (a) cycles performed every 2–3 days and (b) additional cycles performed every hour.

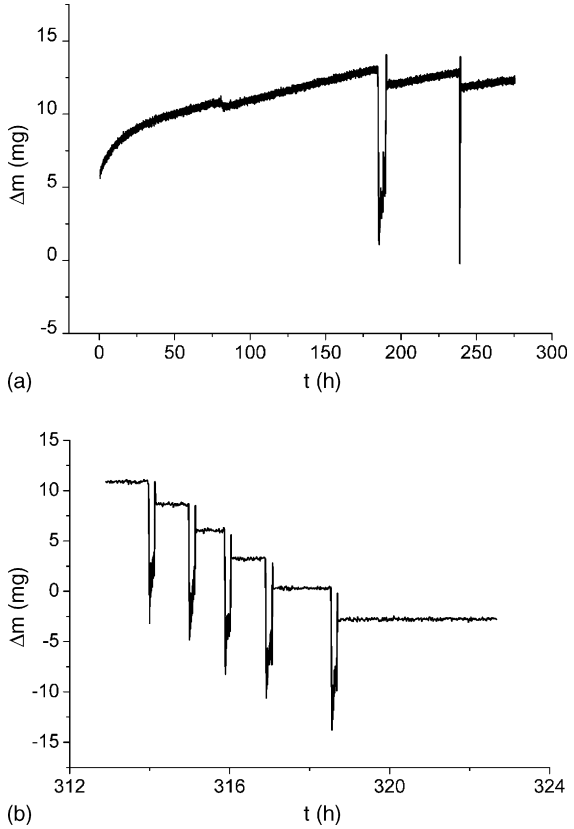

Fig. 3. Cyclic oxidation curves for samples electrophoretically coated with mullite and additional mullite/Al_2O_3 layer at 1550 °C: (a) cycles performed every 2–3 days and (b) additional cycles performed every hour.

The SEM image of a typical sample after cyclic thermogravimetric experiments at 1500 °C is shown in Fig. 4. In order to prepare the cross-section of the sample for SEM it was necessary to deposit a Ni layer on the top of it. From this image, it is obvious that the previously deposited coating system composed of mullite/Al_2O_3 is continuously mixed with SiO_2 growing underneath due to passive oxidation of SiC. According to Schmücker and Schneider,[5] the grains in Fig. 4 correspond to mullite, which was also confirmed by means of EDX analysis. This means that beneath the eutectic temperature in the Al_2O_3–SiO_2 phase diagram[3] a glass phase is formed from which mullite crystallizes[6] on cooling down. The additional Al_2O_3 in the coating thus serves as a reservoir for mullite formation by reaction with the SiO_2.

As mentioned above, an average mass loss of 2 mg per cycle was observed for all investigated samples. Therefore, this mass loss must be correlated with the velocity with which the cracks in the SiC layer open and close. These cracks originate from the CVD process and tend to close at temperatures above the CVD processing temperature (≥1100 °C). On heating from room temperature these cracks are open and the C/C–Si–SiC substrate starts to burn above 400 °C.[7] On approaching 1100 °C, the cracks in the SiC layer tend to close decreasing the oxidation rate of the substrate. One could also imagine that additional cracks can be formed on cooling down the sample due to different thermal expansion coefficients in the SiC layer leading to further burn-out of the substrate.

At this point it was interesting to check, if these processes take place in the same temperature region during heating and cooling. Therefore, we simulated one cycle in a furnace equipped with a quadrupole mass spectrometer (QMS, Pfeiffer OmniStar™ GSD 301 gas measurements possible at pressures up to 10^5 Pa, Fig. 1) under oxygen flow. The sample used was five times coated with a mullite layer and additionally coated from mullite/Al_2O_3 suspension as described in Section 2. According to the experimental results (Fig. 5), it is obvious that the complete burn-out of the substrate took place during heating the sample in the temperature range from 500 to 1000 °C with a small fraction during dwelling at 1300 °C for 2 h. On cooling down no oxidation products as CO and CO_2 were detected. This means that on cooling the thermal stress owing to the difference in thermal expansion coefficients between the substrate and the protective

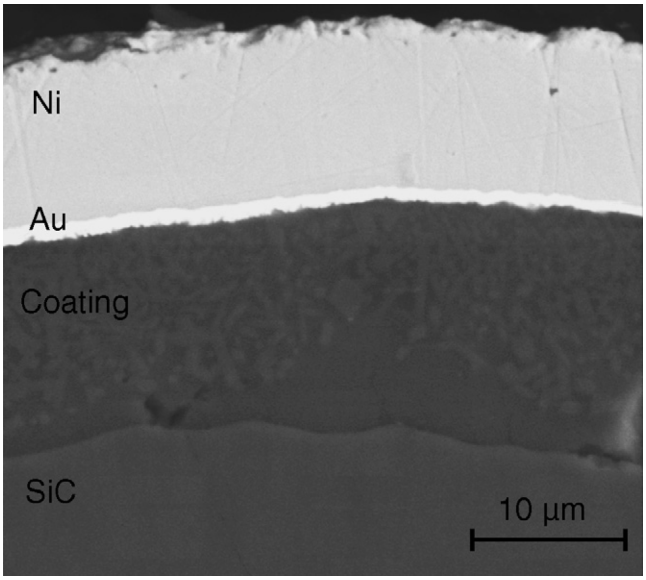

Fig. 4. SEM image of sample after cyclic thermogravimetric experiment at 1500 °C. Additional Au and Ni are protective layers for a proper preparation of cross-section. Bright grains in the coating have the composition of mullite and the dark region is a SiO_2-rich matrix.

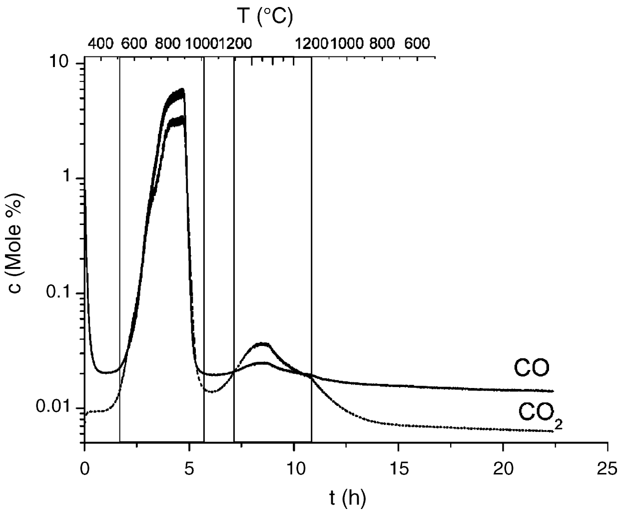

Fig. 5. QMS diagram of burn-out products for cycle simulation in a flow of O_2.

layers (SiC/SiO_2/mullite) is not high enough to form again the cracks in the same temperature range. At lower temperatures (obviously below 500 °C), this thermal stress is high enough and leads to the cracks observed at room temperature, but the oxidation reaction is slow or practically not existing so that no burn-out of the substrate could be detected.

Based on these results, it is assumed that during the cyclic experiments the burn-out of 2 mg per cycle takes place on heating up the sample from room temperature to the oxidation temperature. Because of the different experimental conditions one is not allowed to make direct comparison of the mass losses in both cases.

4. Conclusions

Electrophoretically deposited mullite layers offer substantial protection of C/C-Si-SiC substrates against oxidation at temperatures between 1200 and 1550 °C. At temperatures above 1550 °C this protection is significantly reduced[2] due to the presence of liquid phase and the formation of CO bubbles. The main task of the present work was to prolong the protectiveness of mullite layers by depositing an additional layer from a suspension of mullite precursor with 5 wt.% of Al_2O_3 powder. The added Al_2O_3 serves as a reservoir for the growing SiO_2 layer. Oxidation experiments under cyclic conditions at 1500 and 1550 °C yielded encouraging results. It was possible to perform several cycles without reducing the protectiveness of the coating system. The observed weight loss of about 2 mg per cycle could be attributed to the open cracks in the SiC layer during heating up from room temperature. These data should allow to develop a model that can describe the mechanism of sealing and crack propagation between room temperature and the critical temperature of crack closure in the SiC layer (about 1100 °C).

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