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Yttrium silicate coating system for oxidation protection of C/C–Si–SiC composites: Electrophoretic deposition and oxygen self-diffusion measurements

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Abstract

Yttrium silicate (YSI) coatings are promising complements to SiC coatings for protecting C/C–Si–SiC composites against oxidation owing to the pronounced chemical and mechanical properties of this material (low Young's modulus, low thermal expansion coefficient, low evaporation rate and oxygen permeability, good erosion resistance). Under control of deposition voltage and duration, yttrium silicate coatings of various thicknesses were electrophoretically deposited from powder suspensions. The protectiveness of these coatings was tested by means of thermogravimetric analysis in air. Diffusion data for oxygen in yttrium silicate needed to correlate the experimentally obtained oxidation rates in a phenomenological model were obtained by the IEDP (isotope exchange depth profiling) method from tracer diffusion measurements in single crystalline yttrium silicate and compared to diffusion data in mullite.

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1. Introduction

Silicon carbide infiltrated carbon–carbon composites show exceptional mechanical properties at high temperatures which makes them a promising material for aeropropulsion applications where temperatures may exceed 2000 °C.[1] Unfortunately they exhibit a very low resistance against oxidation in oxygen containing environments at temperatures above 400 °C. Therefore C/C–SiC materials are initially coated with a SiC layer. Due to high processing temperatures of chemical vapor deposition of the SiC layer many cracks develop in this layer after cooling down to room temperature and limit its oxidation resistance at higher temperatures.[2,3] Therefore it is necessary to apply a multilayer coating system in order to improve the oxidation resistance of the C/C material and to extend its service time.[4–7]

Ogura et al.[8] were among the first who proposed yttrium silicate as an oxidation protection system for C/C composites. Yttrium silicate seems to be one of the best candidates for a coating material for carbon–carbon composites because of its excellent properties such as a thermal expansion coefficient similar to that of SiC, a low evaporation rate and a low permeability for oxygen.[9]

Webster et al.[10] and Aparicio and Durán[11] have prepared protective layers by dip coating of C/SiC samples in an aqueous slip made of a mixture of yttrium oxide and silicon dioxide powders.

In our previous works[12–15] we used electrophoretic deposition (EPD) to produce mullite layers for extended oxidation protection of C/C–Si–SiC composites[12–14] as well as electrodes and electrolytes for solid oxide fuel cells.[15]

The aim of this work was to prepare yttrium silicate powders and to use them for the production of protective coatings by means of electrophoretic deposition. The efficiency of these coatings against oxidation was characterized by means of isothermal thermogravimetric analysis. Tracer diffusion experiments were also performed in order to estimate oxygen self-diffusion coefficients in the bulk, which are needed for a better understanding of the transport mechanisms in yttrium silicate and for service time prediction of the coatings. This kind of diffusion measurements in Y_2SiO_5 single crystals has to our best knowledge never been done before.

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2. Experimental

The sol–gel method can be used to produce fine-grained yttrium silicate powders[16] but is experimentally more complicated as compared to the combustion method. The YSI powders were prepared by a modified Pechini method, which allows the preparation of fine and homogeneous powders as reported in our previous work.[17] Crystalline powders of yttrium mono- and disilicate (Y_2SiO_5 and $Y_2Si_2O_7$) were obtained at 1100 °C.

The produced powders were further used separately or as a mixture (70 wt.% $Y_2Si_2O_7$ and 30 wt.% Y_2SiO_5)[11] for the production of dispersions in isopropanol suitable for electrophoretic deposition.[15,17]

Electrophoretic deposition was performed onto metallic substrates (dimensions: 10 mm × 10 mm × 1 mm) and on C/C–Si–SiC composite substrates (Schunk Kohlenstofftechnik GmbH, Heuchelheim, Germany) in the form of thin slabs with average dimensions 20 mm × 20 mm × 2 mm.

The preliminary experiments on the metallic substrates were performed as described earlier[17] in order to optimize the conditions of deposition regarding the deposition rate and the quality of the deposited layers. The results of this optimization procedure are shown in Fig. 1.

The best deposition conditions for all systems (dispersion of pure Y_2SiO_5 or $Y_2Si_2O_7$ in isopropanol and dispersion of the yttrium silicate mixture composed of 70 wt.% $Y_2Si_2O_7$ and 30 wt.% Y_2SiO_5) were found to be 60 V/1–3 min.

At these conditions it was possible to obtain coatings with an average thickness of 5 μm/deposition step at 60 V/1 min. Multiple depositions were also possible. The total starting thickness of the protective yttrium silicate layers was between 15 and 30 μm for the deposition conditions 60 V/1 min (three EPD cycles), 60 V/2 min and 60 V/3 min (one EPD cycle), respectively.

For the measurement of the tracer diffusivities in yttrium silicate single crystals were used. The single crystalline samples were supplied by Toplent Photonics, Australia. The samples were first annealed at 1530 °C in order to reduce stresses and to heal up fast diffusion paths caused by the polishing procedure. Afterwards each sample was put in the furnace and equilibrated at the diffusion temperature ($1150\,°C < T < 1530\,°C$) in an $^{16}O_2$ atmosphere ([]) for a period at least 10 times longer than the diffusion time. Afterwards the atmosphere was rapidly (within 30 s) changed from $^{16}O_2$ to $^{18}O_2$ and the diffusion experiment was started. After the annealing time the sample was immediately quenched by pulling it out from the hot zone of the furnace with a manipulator.

The samples were analyzed by means of secondary ion mass spectrometry (SIMS). A Cameca IMS 5f SIMS was used for depth profiling with Cs^+ as the primary beam. To limit the charging effects, all samples were carbon coated and additionally an electron flood gun was used in conjunction with the primary beam. The depths of the craters were measured after the SIMS experiments using an Alpha Step 500 surface profiler with a resolution of ∼5 nm. Assuming uniform sputtering, the time data obtained from the SIMS can be converted to distance data using the results from the crater depth measurements. The typical area of the craters was 150 μm × 150 μm.

3. Results and discussion

3.1. Thermogravimetric analysis

The protectiveness of the deposited layers was tested in a thermobalance isothermally in air at 1500 °C (Fig. 2).

Although the deposited layers were not completely dense after sintering at 1400 °C thermogravimetric analysis showed oxidation protection (mass gain) for over 100 h. A mass gain means in this case, that the deposited layer really protects the C/C composite.

If the oxygen which diffuses through the protection layer reacts only with the SiC layer, then after the oxidation reaction: $SiC + 1.5\ O_2 \rightarrow SiO_2 + CO$ we have a mass gain of 20 g/formula unit, which overcompensates the mass losses due to CO release.[12–14] In this case the overall procedure is called "passive oxidation" of the C/C–Si–SiC composite. If the oxygen reaches the carbon fiber through cracks or because of the failure of the protective layer, then the overall procedure is called "active oxidation" of the C/C–Si–SiC composite and is followed by a mass reduction of the sample.[12–14]

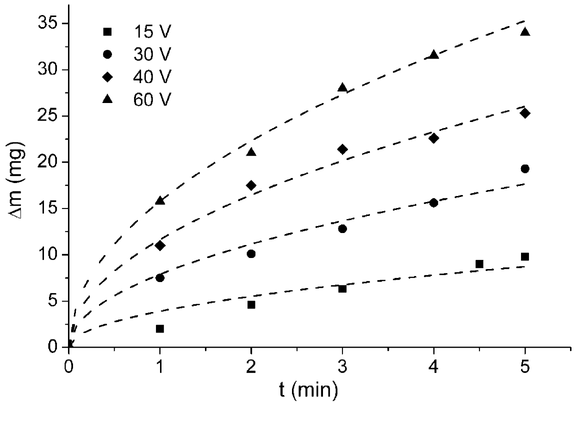

Fig. 1. Deposited mass as a function of deposition time and deposition voltage for yttrium silicate suspension in isopropanol.

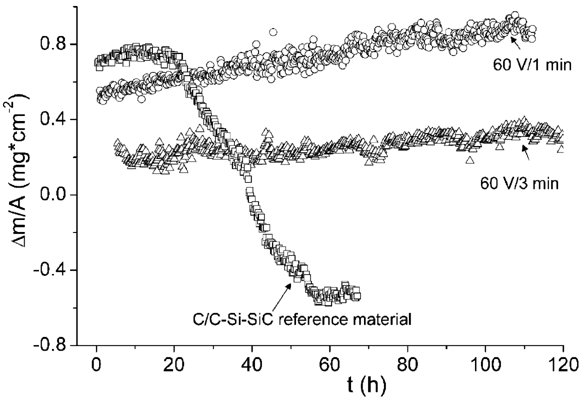

Fig. 2. Raw data for the mass increase of reference material and with yttrium silicate mix (70 wt.% Y_2SiO_5 and 30 wt.% $Y_2Si_2O_7$) coated C/C–Si–SiC substrates during TG-analysis at 1500 °C in air.

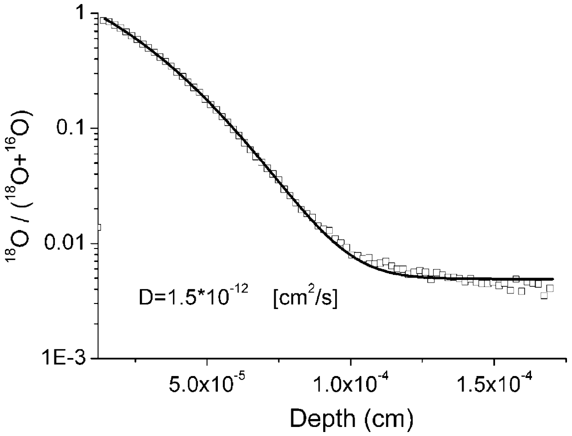

Fig. 3. Representative oxygen diffusion profile in single crystalline yttrium silicate after annealing for 6 min at 1505 °C in 200 mbar $^{18}O_2$. Solid line represents a fit of the data (open squares) according to Eq. (1).

3.2. *Oxygen diffusion in single crystalline yttrium silicate*

Diffusion data in the protective layer are needed in order to be able to understand the mechanism of the oxidation of C/C composites protected by yttrium silicate layers. From oxygen isotope exchange experiments in single crystalline materials one obtains the bulk diffusion coefficient. Assuming that the surface exchange coefficient is high in the temperature regime of the oxidation experiments (in Fig. 3 a surface concentration of about 90%, which is almost the 18-O concentration in the gas phase, confirms a high rate of the surface exchange reaction) then the diffusivity of the oxygen ions in the bulk is together with the grain boundary diffusivity the most important transport parameter. For evaluation of the grain boundary diffusivity in polycrystalline samples, one needs the bulk diffusivity, which can be estimated from experiments in single crystals or together with the grain boundary diffusivities from carefully performed diffusion experiments in polycrystalline samples.[18]

Exemplarily the raw depth profile data of a sample annealed at 1505 °C for 6 min are shown in Fig. 3.

By fitting the raw data according to Eq. (1) we obtain the tracer (self)diffusion coefficient D in the bulk yttrium silicate:[19]

$$C = C_0 + (C_s - C_0) \times \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \tag{1}$$

The first results show a high activation enthalpy of about 3.5 eV and slow oxygen diffusivities, for example 1.5×10^{-12} cm^2/s at 1505 °C. These oxygen bulk diffusivities are about two orders of magnitude higher than the corresponding bulk diffusivities in single crystalline 2/1 mullite.[20] This means that yttrium silicate is a suitable oxygen diffusion barrier but not as effective as mullite. The advantage of yttrium silicate coatings as oxygen diffusion barriers seems to be the higher service temperature due to higher melting and eutectic temperature of this system.[21] The difference of two orders of magnitude in the bulk diffusivities of Y_2SiO_5 and mullite also implies, that the thickness of Y_2SiO_5 layer should be at least 10 times thicker than that of the mullite coating layer, if oxygen bulk diffusion is the rate determining step.

4. Conclusions

It was possible to prepare stable yttrium silicate and yttrium disilicate powder suspensions in isopropanol. After addition of iodine these suspensions were suitable for electrophoretic deposition. According to isothermal thermogravimetric analysis electrophoretically deposited yttrium silicate coatings, although not completely dense, have protected the C/C–SiC substrate against oxidation for over 100 h at 1500 °C.

SIMS measurements of the oxygen tracer diffusion showed that the oxygen bulk diffusion in single crystalline yttrium silicate is higher than in mullite.[20] These preliminary results indicate that it should be beneficial if the coating system based on yttrium silicate finds its application at higher temperatures (above 1550 °C) as a supplement to mullite coatings.[12–14] At lower temperatures according to our diffusion experiments mullite is more effective as an oxygen diffusion barrier than yttrium silicate.

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